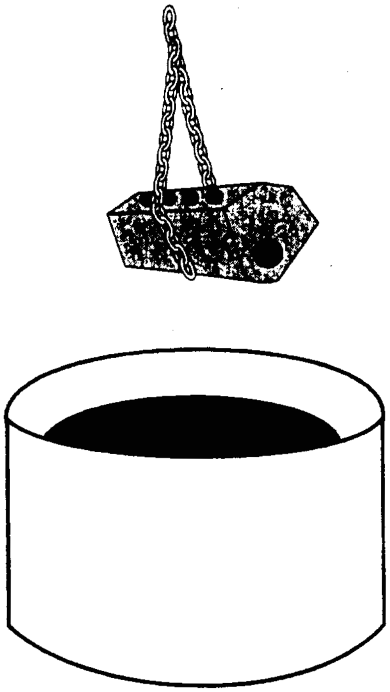
Parts Cleaning

Pollution Prevention Information Packet



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Prepared by

Office of Pollution Prevention
Ohio EPA
P.O. Box 1049
Columbus, OH 43216-1049
(614) 644-3469

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Parts Cleaning
Pollution Prevention Information Packet

Can you use more information about making your cleaning operations more profitable? More likely to be in compliance, or better? More environmentally friendly, using pollution prevention? And, who sells the necessary equipment and materials? Would you like to get the basics in one place? Ohio EPA's Office of Pollution Prevention has done some of that work for you. This packet has several of the best, most beneficial and commonly referenced technical papers available in this area. We are pleased to provide this information to help make your job easier.

Pollution prevention offers you some of the best opportunities to reach each of your objectives above. Please use these references as guidance, and contact the Office of Pollution Prevention if you would like further information.

The information packet contains the following **articles**:

Introduction

1. Kuhn, A.T. 1993. *Is it Clean? Testing for Cleanliness of Metal Surfaces.* Metal Finishing 91(9):25-31.

2. Jones, W.C. 1985. *Testing Surface for Cleanliness.* Metal Finishing 83(10): 13-15.

3. Fromm, C.H., S. Budaraju, and S.A. Cordery. 1988. *Minimization of Process Equipment Cleaning Waste.* Solvent Waste Reduction Alternatives Seminar: Speakers Notes. CERI-88-06. U.S. Environmental Protection Agency, Center for Environmental Research and Information and Office of Solid Waste and Emergency Response, Washington, D.C. 17pp.

Alternatives in General

4. U.S. EPA. 1994. Guide to Cleaner Technologies: Alternatives to Chlorinated Solvents for Cleaning and Degreasing. *Available Technologies for Alternatives to Chlorinated Solvents for Cleaning and Degreasing: Descriptive Aspects and Operational Aspects (Tables 2 and 3).* EPA/625/R-93/016. U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C. 5pp.

5. New Jersey Technical Assistance Program. 1994. *Know Your Cleaning Alternatives.* The Catalyst 1(2):4-5. New Jersey Technical Assistance Program, Newark.

Aqueous & Semi-Aqueous Cleaning

6. Michigan Departments of Commerce and Natural Resources. 1994. *Aqueous and Semi-Aqueous Cleaners.* Fact Sheet #9409. Environmental Services Division, Michigan Departments of Commerce and Natural Resources, Lansing. 16pp.

7. Durkee II, J. 1994. *Semi-Aqueous Cleaning: Is It For You.* Products Finishing 59(1): 62-68.

8. Ohio EPA. 1995. *Extending the Life of Aqueous Cleaning Solutions.* Fact Sheet No. 31. Office of Pollution Prevention, Ohio Environmental Protection Agency, Columbus. 6pp.

Pollution prevention means the use of source reduction techniques in order to reduce risk to public health, safety, welfare and the environment and, as second preference, the use of environmentally sound recycling to achieve these same goals. Pollution prevention avoids cross-media transfers of waste and/or pollutants and is multi-media in scope. It addresses all types of waste and environmental releases to the air, water and land.

Other Alternatives

9. U.S. EPA. 1994. Guide to Cleaner Technologies: Organic Coating Removal. *Available Cleaner Technologies for Coating Removal: Descriptive Aspects and Operational Aspects (Tables 1 and 2).* EPA/625/R-93/015. U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C. 6pp.

10. Konopka, J.E. 1987. *Gentle Blast: Plastic Blast Media Removes Paint and Surface Soils Without Harming Substrates.* Products Finishing 51(11): 74-81.

11. U.S. DOE. 1994. *Supercritical CO_2: An Environmentally Acceptable Alternative for Industrial Cleaning Applications.* Industrial Innovations for Tomorrow. Office of Industrial Technologies, U.S. Department of Energy, Washington, D.C. 2pp.

12. U.S. EPA. 1994. Guide to Cleaner Technologies: Alternatives to Chlorinated Solvents for Cleaning and Degreasing. *Available Technologies: Supercritical Fluids.* EPA/625/R-93/016. Environmental Protection Agency, Office of Research and Development, Washington, D.C. 4pp.

13. U.S. EPA. 1994. Guide to Cleaner Technologies: Alternatives to Chlorinated Solvents for Cleaning and Degreasing. *Available Technologies: Carbon Dioxide Snow.* EPA/625/R-93/016. Environmental Protection Agency, Office of Research and Development, Washington, D.C. 3pp.

14. *Durkee II, J.B. 1995. *Regulations Affecting Aqueous Cleaning Systems.* Products Finishing 59(8): 100-102.

A listing of **potential vendors** can be found at the end of the information packet. This list is not necessarily a complete listing of vendors, but is being provided to help identify and locate vendors of pollution prevention equipment and supplies. Ohio EPA does not endorse any of these vendors, but provides this information as a service to Ohio businesses.

The U.S. Environmental Protection Agency's Enviroene is a useful tool when selecting an alternative solvent. Enviroene is host to a computerized expert system known as the Solvent Umbrella. The Solvent Umbrella allows users to find alternative solvent information through a single, easy-to-use command structure. In particular Enviroene provides a link to the Solvents Alternatives Guide (SAGE). SAGE is an expert system that initially evaluates the user's current operating scenario. Next SAGE identifies possible alternative solvent chemistries and processes that best suits the defined operating and material requirements. Enviroene is accessible through the Internet at http://es.inel.gov or by modem at (703) 908-2092. SAGE is accessible within the Solvent Substitution Data Systems section of Enviroene.

Besides this information packet, the Office of Pollution Prevention (OPP) of Ohio EPA provides other types of technical assistance. OPP provides industry specific pollution prevention from over-the-phone consultations to on-site pollution prevention assessments. All services are non-regulatory and provided free-of-charge. OPP also coordinates voluntary pollution prevention programs such as Green Lights and Ohio Prevention First. In cooperation with the Ohio Department of Development, OPP administers a pollution prevention loan program. This program loans funds for existing facilities to acquire or renovate machinery and equipment for pollution prevention practices. For further information on any of OPP's program contact OPP at **(614) 644-3469**, or point your Internet World Wide Web browser to: http://www.epa.ohio.gov/opp/oppmain.html.

Is It Clean? Testing for Cleanliness of Metal Surfaces

by Anselm T. Kuhn,
Finishing Publications Ltd., Stevenage, Hertfordshire, England

Kuhn, A.T. 1993. *Is it Clean? Testing for Cleanliness of Metal Surfaces.* Metal Finishing 91(9):25-31. Reprinted with permission from Elsevier Science Inc.

CLEANLINESS: UNGLAMOROUS BUT VITAL!

Regular readers of *Metal Finishing* would probably find it impossible to locate a single issue of the journal in which, one way or another, the cleaning of metals prior to their subsequent surface treatment is not mentioned somewhere. Expert after expert delivers the same simple message—poor cleaning is the most common single cause of defect incidence or coating failures. Among the most common failures from poor cleaning, we can mention poor adhesion of coatings, poor corrosion resistance, blistering and pitting, failure to pass specification/standards tests and stained and/or irregular coatings.

To make matters worse, very few metal-finishing processes today are based on a single coating. Duplex metal coatings, metal plus conversion coatings or metal plus organic coatings are commonly found combinations. When these fail, it is mostly the outer layer that manifests the failure—but what is the real cause? All too often, it goes right back to the lowest of the coatings—and the cause is incorrect cleaning. Troubleshooting such situations is an exercise most finishers (except those who fancy themselves as "private eyes") can do without.

All of the foregoing is as true today as it has been since finishing began; but thanks to new environmental legislation, nearly all metal finishers in the United States and Europe have changed (or are about to change) their cleaning technologies. This might mean new equipment using traditional organic chlorinated solvents, such that their escape into the atmosphere is controlled. It might mean new organic solvents, such as terpenes, or aqueous or semiaqueous cleaning systems. Metal finishing has been getting mixed messages on this front. Some finishers who have converted to aqueous or semiaqueous systems have expressed themselves as totally satisfied. Others grudgingly accept that the new methods will do the job but still consider that solvent cleaning gave a cleaner surface or was more "forgiving" to operate as a process. We have even heard of a handful of plants that, having made the switch, reverted to solvent cleaning after what they saw as a disastrous experiment. Whichever the case, now more than ever, metal finishers should be on their toes and asking themselves, "Is it clean?"

What Do We Mean by "Clean"?

The answer to this question depends on the metal-finishing process sequence being used. The most common form of surface contamination is oils or greases that originate from mechanical processing, such as rolling, or are deliberately applied as a temporary protective coating for storage or shipping. Mold-release agents are another source of such films and, if based on silicones, are arguably the most difficult to remove of all such films encountered by the finisher. Films of organic coatings such as these are bad news for nearly all metal-finishing processes. The only exception that comes to mind involves solutions containing strong oxidizing agents such as chromic acid, so chromium plating (but not the nickel deposition that usually precedes it) and chromic acid anodizing are two treatment processes that can probably tolerate the presence of organic film contaminants, although, even here, no one is suggesting that this should be put to the test.

Other forms of surface contamination can broadly be classified as "chemical" (e.g, oxides) or "particulate" (dust). Of these, one can make the following comments. Oxides and hydroxides will be removed by cathodic cleaning, by pickling or indeed by the cathodic nature of electrodeposition processes themselves. Particulates can give rise to plating problems, causing rough deposits and sometimes pits; however, unlike organic films, they can readily be seen either with the naked eye or with a low-power magnifying glass. Ascertaining their presence on the surface therefore presents no great challenge. In short, in mainstream metal finishing, the presence of organic films is both inimical to successful finishing and difficult to detect.

In the printed circuit board (PCB) and related industries, organic contamination as described above is equally undesirable, insofar as electroplating and electroless deposition are key operations; however, a totally different form of surface contamination is no less critical, namely that due to inorganic salts, usually as a result of incomplete rinsing from preceding plating operations. Such residues, on the surface of a PCB, permit the passage of stray ("parasitic") currents that can cause premature failure as a result of corrosion (these salts are frequently hygroscopic). This process is sometimes known as "tracking."

To detect such contaminants, the PCB industry has evolved standard test patterns for measurement of surface insulation resistance. In addition, conductivity measurements of rinse water provide a means by which the danger of low surface insulation resistance values can be signaled. The Institute for Interconnecting and Packaging Electronic Circuits coordinates such standards for the industry. Mainstream finishers in the United States, the United Kingdom and most other countries have no American Society for Testing and Materials specification or similar standard to guide them.

How Clean Should a Surface Be?

There have been various attempts to provide a quantitative basis for measuring surface cleanliness; however, any such units must to some extent depend on the nature of the soil and the method used for its measurement (e.g., chemical or physical). There is thus no simple answer to the question of how clean a surface should be, beyond suggesting that if a suitable test has been found, the results of that test can be matched to the performance of whatever surface treatment is subsequently applied. Without doubt, some processes are far more sensitive to the presence of soiled surfaces than others. In some cases, the actual surface treatment process incorporates its own cleaning action.

Vacuum-based methods are also a possibility for cleaning surfaces. Even in a moderate vacuum, lowering total pressure will increase the rate of evaporation of an organic from the surface, although this may still take many hours to volatilize completely. In electron or ion beam or plasma methods, the surface can be bombarded with ions such as argon that are highly effective in providing a new and therefore clean surface.

As a generalization, it is probably true that water-based coating processes are more sensitive to even monolayers of organic surface contamination than solvent-based paint processes. In the latter case, because there will almost certainly be some mutual solubility between the organic contaminant and the solvent in the paint, the "barrier" effect that operates in the case of aqueous processes will largely disappear.

METHODS FOR MEASURING SURFACE CLEANLINESS

The importance of being able to assess surface cleanliness was recognized early in the 19th century. In surveying the literature on the subject, there is no doubt that a high point was the American Electroplaters and Surface Finishers Society (AESF)-sponsored research project in the early 1950s, headed by H. B. Linford. This project, a model of its kind, started with an exhaustive review of the literature, went on to make a quantitative comparison of the various tests and concluded by suggesting modifications to some of the older methods. The results were published in successive issues of *Plating*[1–13] and were also issued by the AESF in booklet form.

The first industrially significant test for surface cleanliness goes back to the American Civil War, when photographers recognized the importance of having clean glass plates before application of the photographic emulsion to the plate surface.[12] Since then, a number of methods have been developed for measuring surface cleanliness.

- Visual (optical, microscopic)
- Water break
- Spray/atomizer
- Fluorescence
- Contact angle
- Radiotracer
- Stimulated electron emission
- Attenuated total reflection spectroscopy
- Combustion and carbon dioxide analysis
- Surface conductivity
- Scanning electron microscopy
- Auger spectroscopy, ESCA
- Ellipsometry
- Analysis of washings
- Copper displacement
- Dye methods
- Other

These methods can be characterized in two different ways. First, there are complex methods that can only be carried out in well-equipped laboratories. These contrast with the simpler methods that were devised to be used either on the production line or in a very modestly equipped production laboratory. Second, there are methods that indicate only the degree of cleanliness, without offering any insight into the nature of the contaminant, in contrast with other techniques that actually provide a degree of "chemical" information. Examples are (in the first category) techniques that measure wetting or contact angle and (in the second category) attenuated total reflection spectroscopy.

Although the purpose of this report is to provide the most extensive overview possible of such methods, the simpler methods are emphasized. For those with the means and resources to pursue the more complex techniques, the relevant literature is cited.

OVERVIEW OF SIMPLE METHODS

The following methods can usually be implemented without any specialized equipment. They are at best semiquantitative, at worst subjective.

Visual and Optical Inspection

Visual inspection of a bright me surface by eye reveals only the gross soils. Neither passive oxide films r thin layers of grease are thus to be se Ellis[14] mentions such inspection well as that enhanced by the use o hand-held magnifier. Although the l ter enables finer particulate soils to seen, the invisibility of oxide or gre layers remains. Even if an opti microscope is used, this is still tr and although the latter allows partic down to the limit of optical resoluti (governed by the wavelength of lig to be seen, care must be taken t airborne dust particles do not fals the results by settling on the t surface during the examination while the sample is in transit to microscope.

Another visual method is to wipe surface with a paper tissue or a piece white cloth, such as cheesecloth, wh can then be inspected by eye or wit magnifying glass. A white cotton glc can also be used. This approach l been described by Linford and Saul stre.[7] In cases where the sample is bright and smooth, visual examinati is of little use, whereas the wipi method may provide some insights.

Even the simple approach based wiping can be made quantitative, suggested by Brandon.[15] A pressu sensitive tape is used to pick particulate soil and this is then view in a densitometer, which records change in optical density resulti from pickup of the soil.

Wetting Behavior

A clean metal surface is "hyd philic" and will thus be fully "w ted" by water. The presence of gre will prevent this, and, rather th spreading as a uniform thin film, water or moisture will break up i discrete droplets. Passive oxide lay behave no differently from pure me in this respect, and water wetting thus not a test for the presence of su layers. From this principle, a numl of tests have been devised.

Breath Test

Simply by breathing onto a surf and observing the result, a judgment cleanliness can be formed. A cle surface produces a uniform cloudi A greasy one will show droplets.

Water-Break Test

Water is applied to the metal surface, usually inclined at approximately 45° to the vertical. The formation of discrete droplets suggests the presence of hydrophobic impurities on the surface, usually of long-chain hydrocarbons. Lutter[16] points out that another cause may be the use of hard water. Calcium ions can react with long-chain fatty acids to form hydrophobic metal soaps. If this is suspected, the test should be repeated with deionized water. Lutter makes the further point that, in plants fitted with recycled water from an ion-exchange unit, there is the danger that although calcium ions are removed, the concentrations of nonionic surfactants will build up, and these can interfere with the test.

Cohen and Hook[17] make the point that this test will not detect contamination by soaps or surfactants, nor will it detect water-wettable particles, such as rust, oxides or other finely divided metals. In the same way, the presence of surfactants in the water used for this test will interfere with the results. In some cases, the use of water is undesirable because it can cause rapid rusting. Cohen and Hook also mention that the thinner the water film used in this test, the more sensitive it is. Still other weaknesses in this test are due to "bridging" of a small contaminated area by a film of water.

In another version, described by Linford and Saubestre, panels are rapidly removed from the test bath, and the number of seconds for water break to occur are noted. Panels are withdrawn vertically and should be so held above the solution. Alternatively, after withdrawal, they can be inclined at 45°, with water from a wash bottle being applied, thus flooding the surface for approximately 20 sec. Linford and Saubestre[7] suggest that the latter method has a slight drawback because it allows oil to migrate downward during the test procedure.

Spray Pattern or Mist Test

This test, although similar to the water-break test, is less sensitive to the presence of soaps or surfactants and thus forms a better basis for a simple, routine works test. The wetted metal surface is sprayed from a distance of 60 cm with distilled water from a spray gun operated at 0.6–1.0-kg/cm^2 air pressure for 30–50 sec. The resulting patterns are observed. Two variations are described by Lutter.[16] In the first, which increases the sensitivity of this test, the metal is previously etched in 1% hydrochloric acid. In the second, the spray water is dyed with approximately 0.1% of a blue dyestuff.[18] Cohen and Hook[17] describe how the method can be made quantitative by placing a sprayed panel inside a viewing box with a grid of 100 squares and tracing the pattern with a pencil. The number of squares appearing clean are counted, and this procedure is averaged over five panels. The result, expressed as a number (out of 100), was named the "cleanliness index" by Linford and Saubestre.[5] An alternative procedure, described by Linford and Saubestre, is to spray the panel after carrying out a water-break test for approximately 15 sec. Because the panels hang vertically, evaporation to dryness begins at the top of the panel and works its way downward until only drops at the bottom remain. The thickness of the resident water film is thus related to its position on the panel, and the spray pattern test is more sensitive near the top of the panel (where the film is thin). Even the slightest trace of oil droplets near the top of the panel can cause quite widespread areas being formed in the spray pattern, whereas near the bottom, the water droplets only form directly above the oil droplet. This makes the time factor critical. In laboratory conditions, clean areas will typically remain wetted for up to a minute, after which dry patches will appear, initially at the top edge of the panel; however, if spraying is commenced too soon (less than 45 sec after drainage), some areas of potential water break may still be wetted because there is still a fairly thick water film on the surface.

Atomizer Test

This variant of the spray pattern test was devised by Linford and Saubestre.[5] The test is applied to a dry, not a wetted, surface. The resulting wetting action requires a higher surface energy than for the already wetted surface of the spray test. In consequence, this test is more sensitive to the presence of small amounts of grease, etc. Cleanliness can be assessed in terms of the area of wetted surface and also by estimation of the contact angle of residual nonwetted water droplets.[6]

Mercury Droplet Wetting Test

If a droplet of mercury is placed on a truly clean metal surface, it will spread. The presence of grease will cause it to retain a roughly spherical shape. The same is true (and here the mercury behaves unlike water) if oxide films are present at the surface.

Talc Test

The smooth surface to be tested (metallic or nonmetallic) is lowered vertically into a container of water, the surface of which has been dusted lightly with talc. The interaction of the talc particles with the smooth surface is observed. This method has been described by Donelson and Neish.[19]

Another use of talc or lycopodium powder is described by Lutter.[16] This is not used directly as a cleanliness test but to detect the presence of oily layers on the surface of a cleaning bath. It will be evident that where such layers are present, however much a metal is cleaned by immersion in solution, on being raised from the cleaning solution, it will pass through such oily films and be contaminated by them. According to Lutter, when paraffins or other nonpolar hydrocarbons are present on the surface, they form spherical or lens-shaped globules. In the presence of polar substances, such as drawing lubricants, the hydrophobic dust particles are displaced.

Copper Displacement Test

If a metal such as steel is immersed in an aqueous solution of copper sulfate, a so-called "displacement reaction" will take place—a pair of coupled electrochemical reactions in which the less noble metal (the steel) is anodically dissolved, to be replaced by the more noble metal (copper) depositing from solution. The old school trick of immersing a copper coin in a solution of silver nitrate to produce a silver coating is another example. If, however, the metal surface is obscured by a layer of grease, this exchange reaction will be impeded or may not take place at all. Linford and Saubestra recommend the following solution composition: 63 g/L copper sulfate (pentahydrate) and 17 g/L sulfuric acid.

The panels are dipped rapidly into solution, held motionless for 10 sec and then removed rapidly and transferred to a beaker of distilled water in which they are agitated for 15 sec. They are then hung vertically, washed for 20 sec with water from a wash bottle and allowed to dry, preferably using radiant heat from a bright light source, for example. Ether extraction is used to remove any remaining oil patches, and the panels are then examined.

Potassium Ferricyanide Test (Ferrous Surfaces Only)

Rag-bond paper is cut into strips approximately 6 × 12 cm. It is coated on one side with a solution of 50 g/L crystalline white gelatin and 50 g/L sodium chloride (chemically pure grade will do). The strips are laid flat on a sheet of glass, and a glass rod, dipped in solution, is rolled from one side to the other. This process is repeated four times. The paper is then allowed to dry and can be stored ready for use. Before testing, the paper is soaked for up to half an hour in the following solution: 50 g/L sodium chloride, 10 g/L potassium ferricyanide and 1 g/L hydrochloric acid. Linford and Saubestre[7] make the point that it is wise to include acid in the above formulation because, should it be omitted, the blue color formed tends to be streaky and light, making the identification of oily patches difficult.

The test piece (a metal panel) is laid flat on a piece of glass, and the impregnated paper is applied to its surface, with the gelatin-coated side in contact with the metal. A glass rod covered with an 8-cm length of rubber tubing is rubbed briskly over the metal surface for approximately 15 sec. Additional test solution is poured over the paper until it is completely remoistened. After 3 min of contact, the paper is removed and allowed to dry. Clean areas will be relatively dark blue on the test paper, whereas oil-contaminated regions will appear as colorless or yellowish zones. No notice should be taken of the odd streakiness in blue zones, which may be due to poor surface contact, bad drying or oxidation. This is especially true with respect to the areas close to the edges. If the time of contact is too long, the blue color will partly disappear.

Linford and Saubestre suggest an alternative procedure (generally less satisfactory), and this is to dip the panel, after testing, into 1 vol % hydrochloric acid and study the blue pattern. Pollack and Westphal[20] quote, as a source of information, an article by Macnaughton.[21]

Fluorescence Test

Some mineral oils and greases will fluoresce in UV light, and this has been used as a quantitative means of estimating the amounts present.[22] For those greases (mainly animal or vegetable) that do not themselves fluoresce, use of a hydrocarbon-soluble indicator dyestuff may be made. Typically, UV radiation of approximately 365 nm is used. In its crudest form, a subjective assessment can be made using commercially available UV light sources. To place the test on a quantitative basis, the results are photographically recorded, using a UV filter. The sensitivity of the method is linked to the length of the photographic exposure, which can range from 1 min to 1 hr. Such time extension increases the sensitivity by approximately 15 times and allows residues of some 0.12 g/m^2 to be measured.[23] Since the time that this sensitivity was quoted, there have been advances in both film sensitivity and fluorescence activity of dyes. One would therefore expect even lower amounts of soil to be detected.

Linford and Saubestre[7–9] used both mineral and lard oils to test degreasing procedures, and both of these are only faintly fluorescent in UV. They therefore used the dye fluorescent green HW. Although this is described as being "oil soluble," they found it impossible to dissolve sufficiently high concentrations and therefore resorted to an indirect technique. Approximately 1.7 g of dye was dissolved in 50 ml of solvent (Linford and Saubestre used benzene, which would almost certainly be prohibited today). This solution was then heated over a water bath until its volume was reduced to approximately 8 ml. A refluxing action down the container walls prevented crystallization of the dye. This concentrated solution was clear, dark red and free-flowing. While it was still hot, some 400 ml of oil was added to the beaker, and this solution was used for testing. In the case of mineral oil, some precipitation was occasionally seen after a few days, and this was removed by decantation or similar methods. Animal fats did not produce simil solids.

Lutter[16] makes the point that b cause such a wide range of organ compounds fluoresce, the presence dust particles can interfere. Likewis many surfactants will fluoresce, ar these will give false indications eve where they are present as fully wate soluble species. A further criticism the test is that hydrocarbon-solub dyestuffs can be water solubilized t synergistic effects (i.e., made hydr philic). In consequence, the degreasir solution and, equally, the adhere water layer on the test sample beir withdrawn from it, may contain suc water-solubilized dyestuffs, which, b cause they fluoresce, will again inte fere with the test.[24]

Dye Test

This test, again described by Lu ter,[16] seems little known outside Ge many. A sample of the cleaning sol tion is placed in a beaker and raised its prescribed operating temperature. sample of metal for degreasing is the introduced. As a result, the heavy sc components (some inorganic, son organic) settle at the bottom of tl beaker, whereas lighter oily comp nents float on the surface. An oi soluble, water-insoluble dye is the added, such as Sudan blue. This colo the hydrophobic phase as well surface films of metal soaps or mon molecular layers, rendering them vis ble. The bath is then stirred, using magnetic stirrer. To facilitate compar son, a constant stirring speed should l set. By study of the system, especial from the size of the droplets of tl blue-dyed oily phase, the surface e ergy and thus the cleaning efficacy the solution can be judged. The small the droplet size, the better it is. Aft stirring is switched off, the time for tl emulsion to re-form is noted. Bat with strong cleaning effect can mai tain the oil droplets in suspension f longer or even maintain the emulsifi state, as shown by cloudiness of tl solution. Depending on the type cleaning solution used, emulsions c be stable for hours, even days, befo breaking up to give a discrete oi phase.

High-capacity cleaning baths a characterized by a transparent a stable blue-colored colloidal solutio the presence of which can be verified by a Tyndall effect. A further refinement of this test is as follows. A sample of the work being cleaned is withdrawn from the solution. The dyed liquid droplets should all roll off the surface; residual oil droplets can be easily detected thanks to their color. The volume of cleaning solution dragged out in this way can be easily determined by colorimetry.

Yet another variant of this dye test can be carried out by dyeing the cleaning solution yellow, using a color that is totally insoluble in the oily phase. Magnetic stirring is applied, and, in the presence of the finely divided blue-colored droplets, a complementary green color is seen in solution, at times only transiently. As soon as the stirring is stopped, this vanishes. Cleaning baths not suitable for practical use are those in which the blue oily phase rapidly separates from the yellow aqueous phase, rising to the surface.

Emulsion-type baths tested in this way give a milky cloudiness with a green-colored emulsion; high-capacity baths, in contrast, give a totally transparent green solution that is stable for extended periods of time. Only when such baths have reached maximum oil uptake capacity does a discrete blue-tinted upper layer form on the surface.

High-capacity cleaning baths that contain emulsifying agents, solution promoters and hydrotropic substances must first be tested to determine whether they are capable of solubilizing dyestuffs that are normally insoluble in water.

Lutter[16] suggests that the dyestuff tests described above are close to actual conditions, and in addition require little time or materials to carry out. They provide insights into the behavior of cleaning baths and also of specific lubricants or pastes used in processing.

Clock Reaction for Copper and Its Alloys

Granata et al.[25] described a simple method, albeit one that is only useful for copper and its alloys. This is based on the so-called "clock reaction." Such reactions, well known to chemists, are homogeneous solution reactions exhibiting a measurable induction period. Strictly speaking, such reactions might better be described as "alarm clock" reactions because, to the outside observer, nothing appears to happen until the "alarm goes off," when there is, for example, a color change. In this case, a solution is made up with 0.025M sodium polysulfide. This is formed by dilution of a 2.66M stock solution. The copper sample is placed in a Petri dish, and the cleanliness is related to the time taken for the sample to turn black; the cleaner the sample, the shorter the time. Granata et al.[25] quote times of 16 sec for freshly abraded copper, increasing to 40 sec after such samples have been exposed to the atmosphere for four days. Formation of oxides on the surface (e.g, by heating in air at 100° C for 6 hr or immersion for a day in sodium hydroxide) increases the times to blackening to 75 and 585 sec, respectively. As an alternative to color change, Granata et al. describe how a potentiometric measurement may be carried out using a saturated calomel reference electrode.

Spreading Wetting Test

Jones[26] rightly describes the water-break test as a "go, no-go" procedure and offers an alternative suggestion. A series of solutions are made up, ranging from 80% ethanol and 20% deionized water to one with 1% ethanol and 99% water. These solutions exhibit a range of surface tension from 24.5 (corrected for variations in specific gravity) to 66 dyne/cm. Above this, solutions of potassium carbonate are used to produce (800 g/L) a solution with 101 dyne/cm. By application of a drop of each solution and examination to see whether it forms a bead or a wetting film, surfaces can be "calibrated" with regard to their surface energies.

Another description of the same approach is that by Renaud[27] who uses a range of six liquids of varying surface tension. A known, small volume of each liquid is dispensed (5 µl) from a microsyringe, and the degree of spread is observed. Renaud rightly makes the point that the results of this type of test will depend on whether there is any physical or chemical reaction between the test liquid and the film (if any) on the surface. A further exposition of the method has been given by Cohen and Hook,[17] and Bystry and Penn[28] have also described the use of the method.

Other Simple Methods

Pollack and Westphal[20] list most of the above methods and others as well. These include the following:

1. *Gravimetric test*—one of the least sensitive.
2. *Mears test (Elms modification).* Single drops of an aqueous solution containing 32 ml/L of 30% hydrogen peroxide are applied to a surface, and the time taken for corrosion to appear is measured. The test is described as "not very satisfactory."
3. *Simple contact angle test.*
4. *Oil spot test.* A droplet of degreasing solvent is applied to the so-called clean surface and then evaporated. Formation of a ring suggests the presence of oil.
5. *Rock Island drop test.* Distilled water droplets are allowed to fall from a specified height onto the test surface. The method is said to distinguish between a clean surface and one soiled with a 0.01% oil solution.
6. *Ring test.* A drop of water is formed on the ring of a surface tension tester, and this ring is then lowered to contact the test surface. The process is repeated, and the number of such contacts required to transfer all of the water is noted.
7. *Kerosene viewing of water break.* A wetted panel is dipped into a beaker of kerosene lit from below. Near water breaks are displaced by kerosene, giving a sensitivity better than the usual water break. The sensitivity is said to be equal to or better than the atomizer test.

Of the simple methods that Linford and Saubestre tested and compared, they concluded that the ranking of sensitivity was atomizer > fluorescent dye > spray pattern (water break) > potassium ferricyanide dip > copper sulfate dip. Linford and Saubestre's work, which is too extensive to reproduce or even summarize here, provided comparative data not only for the various methods cited above but, in a second classification, in terms of the type of grease used to contaminate the surface of the metal (e.g., animal or mineral in origin).

Table I. Sensitivity of Test Methods

Method	*Minimum Detectable Residue (g/m^2)*	*Relative Sensitivity*
Fluorescence	0.225	1
Water break	0.022	10
Radiotracer	0.002	110

MORE COMPLEX METHODS

Included here are techniques that do call for some instrumentation, although they require no very expensive equipment.

Radiotracer Method

Radiolabeling was a technique very widely studied and favored from the 1950s onward, when radioactive isotopes first became available. There are probably hundreds of publications (see, e.g., Chapter 21 in ref. 29) in which the adsorption of organic species on a metal surface has been studied. If the first such studies were made in the United States in the 1950s, the great bulk of subsequent work emanates from the Eastern European countries, and although the method appears to have fallen out of favor in the West, it continues to be used in Eastern Europe. The increasing availability of radioisotopes explains the rise in popularity of the method. The subsequent tightening of legislation and regulations governing the use of radioisotopes in laboratories and in industry explains why the method has largely fallen from favor. Indeed, it would not be far from the truth to suggest that for these reasons the method is now only of interest for historical reasons and for very specialized research. As a method for routine industrial use it is fair to state that the procedural requirements involved in the use of radioisotopes make the method more trouble than it is worth. In this spirit, it is worth reproducing the data shown in Table I.[23]

Radiotracer methods had a brief revival in popularity in the form of the evaporative rate analysis method used to characterize the cleanliness of razor blade edges. The essence of the method was to determine the rate at which a test liquid containing a radiotracer element evaporated from the metal surface. As little as 0.02 μg/cm^2 of oil could readily be detected in this way. Typical radiotracers were *n*-tridecane (with carbon-14) or 1,1,2,2-tetrabromoethane. Solvent carriers were cyclopentane, straightforward freons or freons with 10% chloroform. The essence of the method is that, by interactions and mutual solubility, the presence of grease on the surface can inhibit the rate of evaporation. A method was described at length by Andrade[30] and earlier by Hamilton.[31]

Measurement of Contact (Surface) Potential Difference

Guttenplan[32] describes the surface potential difference method, which, unfortunately, once again uses a radioactive source. In this case, the radioactivity is used to initiate ionization. The probe is placed some 1–10 mm above the test surface in air, and the potential difference is electrometrically measured using a high-impedance instrument. The basis for the method is the effect that surface films have on the electronic work function of a metal (energy required to withdraw an electron). In his report, which also cites use of the method to characterize aluminum after conversion coating, Guttenplan compares its sensitivity with the water-break test, finding it easily capable of detecting films that were not shown by the water-break test. The report describes plans to develop a commercially available instrument, but it is not known whether this was ever produced.

Another variant of this method—electrostatic charge decay—measures this quantity and also contact potential difference. It was developed for use on the space shuttle to check the cleanliness of the aluminum surface on the fuel tanks and has been described by Cibula et al.[33]

Combustion Methods

By introduction of a sample of metal to a furnace and passage of oxygen over the surface, oily matter is oxidized to carbon dioxide and water. The former species is determined by one of a number of analytical methods. To ensure complete combustion to carbon dioxide rather than the monoxide, a catalytic stage is included (e.g., usi silver wool and barium chromate). description of the method with typic data, including reproducibility, w published by Kresse et al.[34] The tec nique is not overly sensitive; 5– mg/m^2 was used in this particul work. Oxidation times are typically min and oxidation temperatures a proximately 600°C. The criticism h also been made that soils not contai ing carbon pass undetected by tl method.

Cohen[35] describes a variant of t method used by the Ford Motor Co. follows. A fiberglass cloth saturat with 50% hydrochloric acid is used mop a 4-in. × 12-in. steel panel. Af appropriate drying, the carbon conte is determined by combustion in ox gen at 400 and 600°C, the carb dioxide being determined in one of t usual analytical procedures.

Contact Angle Measurements

Related to the spreading wetti tests above, but more sophisticated its approach, is the actual measureme of the contact angle of a sessile dr which has been mentioned by seve authors, including Cohen[35] and Rice

Washing Tests

A family of tests have been dev oped, mainly by the electronics ind try, in which the surface to be tested washed with an aqueous or nonaq ous solvent. The washings are th subjected to analysis. A trench criticism of this approach is that detects only soil that has been moved, not that remaining on surface. In a sense, it is precisely latter rather than the former that is greatest concern. A full treatment this class of test is given by Ellis.[14]

Analysis of Washings

The simplest method for washi analysis is conductimetric, and this, Ellis describes, has formed the basis several commercial instruments; ho ever, it should be clear that the pr ence of ionic species (acids, alkalis salts, mainly inorganic) is of gre concern to the electronics industry t to the majority of surface treatm processes. That said, such conta nants can interfere with other surf treatment processes, for exam phosphating.

OTHER METHODS

Space does not allow more than a brief mention of other methods. Perhaps the most useful for practical purposes is the optically stimulated electron emission method in which light in the visible or UV region irradiates the surface, and the current resulting from emission of the stimulated electrons is recorded. The method has been described by Chawla[37] and is of special interest because it is the only "modern" instrumental method not involving major financial investment. The use of attenuated total reflection in the infrared region can lead to identification of the actual contaminants. The surface insulation resistance method is best carried out using a standardized "maze" pattern of electrically conducting tracks on an insulating substrate. This is formed by the normal methods used in fabrication of PCBs. Then, too, there are the methods using scanning electron microscopy (enabling density of resident particles to be counted) as well as analytical methods such as Auger electron spectroscopy or electron spectroscopy for chemical analysis. These can, of course, allow inferences to be drawn as to the nature of the surface contaminant, but their use is limited to the largest organizations that have such equipment in-house.

CONCLUSIONS

This report will serve to give some idea of the wide range of test methods for assessing surface cleanliness developed over the years, although it does not claim to be exhaustive. How is a prospective user to choose among them? Clearly, they can be ranked in terms of the cost of equipment or instruments required to carry out such tests. Then, too, the nature of contamination will affect the choice. Particulate soils are not suited to some of the methods described above, and even in terms of oily layers the nature of the oil can be important. The same questions affect the issue of test sensitivity. Linford and Saubestre carried out tests in which the sensitivity of some of the simpler methods was compared. What is undoubtedly true is that the ever-decreasing cost of computer-linked optical scanners or cameras should prompt a reassessment of the methods that previously relied on superimposition of grids to derive a quantitative result. And, most certainly, such is the diversity of methods available that no metal finisher should be able to offer any excuses for processing poorly cleaned work.

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Biography

After majoring in chemistry at Oxford University and receiving a PhD in electrochemistry there, Anselm T. Kuhn worked as an electrochemist for Leesona Moos in New York and then with John Bockris at the University of Pennsylvania. In the United Kingdom, he was a researcher with ICI before starting a career as a university teacher at Salford University and then London University. He is the author and editor of several books and over 100 research publications. Currently he is Managing Director of Finishing Publications Ltd. and Metal Finishing Information Services, both based in Stevenage, U.K. **MF**

Testing Surfaces for Cleanliness

by William E. Jones,
Heatbath Corp., Springfield, MA

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TESTING & CONTROL

INTRODUCTION

The common bond that ties all facets of the metal finishing industry together is the necessity for adequate cleaning prior to the application of the specific coating or treatment. Countless papers on cleaners have been presented, telling what they are, how they work, and the variations in operating conditions necessary to produce the degree of cleanliness required for the specified metal finishing process.

Technical data sheets describing proprietary cleaners always have a section on control of the cleaner. This is usually some form of a titration procedure that, in the case of alkaline cleaners, measures either the free or total alkalinity of the working solution.

While this technique measures the concentration of the solution, it does not measure its effectiveness as a cleaner, even on initial make up, for the specific job it has to perform, nor does it sense the decrease in effectiveness of the cleaner as the soil load increases.

Unfortunately, the most common method for determining that a cleaning problem exists is the appearance of rejected work because of variations in surface quality, irregular coatings, blisters, pits, streaks, or lack of adhesion. All these are familiar indications of a cleaning problem.

Direct measurement of the soil load in a cleaner is not practical since the techniques involved are time consuming and beyond the scope of the industrial metal finishing laboratory. The practical significance of the results obtained would be dependent on a single soil input, a condition which seldom exists.

Obviously, the preferred method for measuring the effectiveness of the cleaning process is to evaluate the cleanliness of the actual metal surfaces that have been cleaned under specific processing conditions.

CURRENT METHODS

Many tests have been proposed for evaluating the cleanliness of a metal surface. Among these are radioactive counting techniques using a tagged component in the soil to be removed.

This is a highly specific method that depends on measuring the cleaner's performance against a soil of known composition. It involves specialized equipment and procedures that are not commonly used in the industry.

The ability of an acidified copper sulfate solution to form a continuous replacement copper coating on a steel surface is sometimes used as a method for evaluating surface cleanliness. It is of limited application and is qualitative rather than quantitative.

Inspection of surfaces under ultraviolet light for fluorescent organic materials is, again, a qualitative technique. Sophisticated analytical procedures to measure the amount of surface carbon on steel test pieces have been advanced as a preferred method, but the equipment is expensive, and the area sampled is small.

The test depends upon the conversion of the small amounts of organic carbon (present in residual oils and soils together with the carbon present in the smut) to carbon dioxide in an oven at controlled temperatures and in an oxygen stream. Operating conditions are maintained so as to prevent the carbon in the steel from influencing the results.

Detection of the small amount of carbon dioxide generated requires special procedures. While carbon is a probable component of most metal surface soils, there is no guarantee of this being true, and a surface showing low carbon does not necessarily indicate a clean surface.

Physical methods have been advanced that attempt to measure the ability of a drop of pure water to wet a cleaned surface. These techniques measure the contact angle between the drop and the surface or the height and/or diameter of a drop of water of known volume on the surface. Again, these procedures require specialized equipment and are more suitable for the research laboratory than for a production control laboratory.

By far, the most common test for surface cleanliness is the "water break" test. A visual evaluation is made of the ability of water to wet the cleaned surface completely without pulling back to form beads of water and leaving unwetted areas. When properly performed, the test should be conducted after the test piece has been acid dipped and rinsed to remove the last traces of any residual alkaline cleaner that would influence the results.

Obviously, this is a go, no-go, type of test that establishes one level of cleanliness as being acceptable for all metal finishing processes. It does not take into account the fact that certain processes require a higher degree of cleanliness than can be detected by this test while other processes may be performed successfully at a lower degree of cleaning efficiency.

BACK TO BASICS

When a surface is cleaned by either physical or chemical methods, or a combination of the two, the net result is an increase in surface energy and a measure of surface energy is a direct measure of cleanliness.

In the liquid phase, surface tension is a direct measure of surface energy. Therefore, a comparison of the surface energy of a metal surface with the surface tension of a liquid, yields a direct measurement of surface cleanliness.

In practical terms, if a drop of liquid of known surface tension is placed on a metal surface and that liquid wets the metal surface and spreads as shown in Fig. 1, this indicates that the surface energy of the metal is *greater* than the surface energy of the liquid.

Conversely, if the drop of liquid of known surface tension remains as a bead and does not spread, as shown in Fig. 2, then the surface energy of the metal is less than the surface energy of the liquid.

A graded series of liquids of known surface tension can therefore be used to measure the surface energy of a metal surface, and therefore its cleanliness, by observing whether or not the liquid wets and spreads on the dried surface of the actual part that has been cleaned.

Fig. 1. Surface tension of test solution is less than surface energy of metal. Solution spreads into irregular pattern.

Fig. 2. Surface tension of test soluti is greater than surface energy metal. Solution retains bead fo and does not spread.

The use of graded sets of liquids of known surface tension has been used in the past to measure the surface wettability of plastics and metals as well as metal cleanliness, but they have been limited to surface tension at or below that of water.

The test procedure herein described extends this range to include surface tension above that of pure water and arranges the surface tension of the test liquids in a geometric progression of 11 steps from about 25 to 100 dynes per centimeter. The composition a properties of the test solutions a shown in Table I.

The ethanol values are based anhydrous ethanol. Reagent gra potassium carbonate was us and solutions were prepared usi deionized water in carefu cleaned glassware.

The apparent surface tensio were measured by the ring meth as depicted in Fig. 3 and correct for specific gravity using stand procedures. The solutions based potassium carbonate were treat with activated carbon and filter

Table I

Solution Number	Composition % by Volume Ethanol	 DI water	Apparent Surface Tension Dynes/cm	Specific Gravity	Corrected Surface Tension Dynes/cm
0	80.0	20.0	27.2	0.850	24.5
1	51.0	49.0	31.2	0.922	28.2
2	33.0	67.0	36.0	0.955	32.7
3	21.5	78.5	41.9	0.970	38.4
4	14.3	85.7	47.3	0.978	43.7
5	9.3	90.7	53.4	0.985	49.7
6	4.5	95.5	61.3	0.991	57.6
7	1.0	99.0	70.1	0.995	66.6
	g/L Potassium Carbonate				
8	220		80.0	1.171	75.8
9	520		91.2	1.377	86.3
10	800		106.7	1.535	101.2

prior to surface tension measurement. The aqueous ethanol solutions require no additional treatment.

The solutions should be stored in clean glass containers. Small glass bottles with a glass medicine dropper closure are convenient for use in performing the test.

To perform the test, the surface should be processed through the cleaning cycle, rinsed, and then dried with a current of clean air. Without delay, a drop or series of drops of one of the test solutions are placed on a horizontal surface of the test piece noting whether it beads or spreads.

There is no need to be concerned with contact angle or droplet height. If the droplet beads, move to the next lower numbered solution and continue moving down one number until a solution is reached that wets the surface spontaneously.

The results are reported as the lowest numbered test solution that can be made to bead on the surface. In evaluating a large area, check a number of different locations as the degree of cleanliness will vary from area to area.

CONCLUSION

This test represents a practical, rapid, economical and sensitive method for the metal finisher to:

1. Control the present cleaning procedures.
2. Monitor the "life" of cleaners.
3. Evaluate competitive processes.
4. Screen incoming surfaces for "difficult to clean" soils. **MF**

Biography

William Jones is research director of Heatbath Corp. He has worked for 35 years as a chemist specializing in the development of nonelectrolytic metal surface treating processes including cleaners, conversion coatings, and molten salt formulations.

Fig. 3. Measuring surface tension to calibrate test solution.

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Minimization of Process Equipment Cleaning Waste

MINIMIZATION OF PROCESS EQUIPMENT CLEANING WASTE

by

Carl H. Fromm
Srinivas Budaraju
Susanne A. Cordery

Jacobs Engineering Group Inc.
HTM Division
251 South Lake Avenue
Pasadena, California 91101

ABSTRACT

The waste associated with cleaning of process equipment is probably a significant contributor to the total waste volume generated by industry. This paper addresses the following aspects related to equipment cleaning waste generation:

- Review of reasons for cleaning process equipment
- Reduction of cleaning frequency
- Reduction of quantity and toxicity of cleaning waste
- Costs associated with cleaning

Equipment cleaning techniques, media, and their applications are reviewed. Reduction of cleaning frequency is addressed in terms of inhibition of fouling through proper equipment design and operation, maximization of equipment dedication, proper production scheduling, and avoidance of unnecessary cleaning. When cleaning has to be performed, the quantity and toxicity of resulting waste can be minimized by reducing clingage, amount of cleaning solution, choice of less toxic cleaning solution, cleaning solution reuse, and other approaches. Application examples are given to illustrate each approach.

INTRODUCTION

The current costs of waste disposal and treatment, regulatory pressure, and concerns about legal liabilities have been forcing U.S. industries to scrutinize their hazardous waste generation practices 1/. A primary objective of these efforts has been to minimize waste generation, i.e. to reduce the quantity and toxicity of the waste.

Of the many industrial waste-generating operations, process equipment cleaning (PEC) is nearly universal in its application, as it is practiced in all segments of manufacturing industry. PEC is of particular importance for discrete processes such as batch reactions, compounding, surface coating operations, etc. This is because the cleaning frequency for discrete processes is generally much higher than for continuous processes. However, this does not mean that cleanup wastes from continuous processes can be ignored. Disposal of sludges from cleaning of heat exchanger fouling deposits, for example, is often of concern to the operators of petroleum refining, petrochemical and chemical process facilities.

The intent of this paper is to review basic waste minimization strategies applicable to cleaning operations. The intent is to provide a structured classification of such strategies presented in the form of a prototype checklist which can be used to help focus and plan a concerted attack on waste.

WHY EQUIPMENT IS CLEANED

Equipment cleaning is a maintenance function typically performed for the following reasons:

- to restore or maintain the operating efficiency of equipment, e.g., to restore adequate heat transfer rate and low pressure drop in heat exchangers.
- to avoid or limit product contamination, e.g., when a paint mix tank needs to be cleaned between batches of varying paint formulations.
- to minimize corrosion and extend equipment lifetime.
- to allow for inspection and repair of equipment.
- to improve appearance (exterior surfaces only).

The need for cleaning is a direct consequence of deposits formed on the surfaces exposed to the process environment. Some of the major routes and origins of deposit formation are summarized in Table 1 along with descriptions and some examples. Understanding how and why the deposits are formed is a critical first step in any waste minimization effort. It is an especially important aspect for equipment and process designers, because the need for equipment cleaning can often be reduced or eliminated through design modifications at minimal expense during the design stage.

A common sense approach to minimizing waste from equipment cleaning operations is to pose and answer the following sequence of questions:

- why is the deposit present?
- how can cleaning be curtailed or avoided (i.e., cleaning frequency reduced)?
- when cleaning is necessary, which cleaning method and medium will generate the least amount of least toxic waste?

Sections below address major aspects related to the last two questions.

REDUCTION OF CLEANING FREQUENCY

Generally, the need for cleaning can be reduced or avoided altogether by the application of the following measures:

- inhibition of fouling or deposit formation rate.
- maximizing dedication of process equipment to a single formulation or function.
- proper production campaign scheduling.
- avoidance of unnecessary cleaning.

Inhibition of fouling is of particular importance in heat transfer applications where it can be accomplished through a variety of means, including use of smooth heat transfer surfaces, lower film temperatures, increased turbulence, control of fouling precursors and proper choice of exchanger type.

TABLE 1. TYPICAL ROUTES AND ORIGINS OF DEPOSIT FORMATION IN PROCESS EQUIPMENT

Route/Origin	Description
Crystallization	Major problem in evaporators and crystalizers (e.g. very frequent in food processing).
Sedimentation	Major problem in petroleum refinery crude unit desalters and oil storage tanks. Also present in cooling tower basins.
Chemical reactions and polymerization	Buildup on the internal reactor surfaces are often encountered (e.g. allyl chloride synthesis). Also of importance in crude oil storage tanks.
High temperature coking	Carbonaceous material depositing on walls of furance tubes (e.g. furnace for ethylene chloride pyrolysis).
Corrosion	Common problem in heat exchangers in chemicals and allied products industry.
Bacterial growth (biofouling)	Major problem on cooling-water-side of heat exchangers in electric power production.
Clingage (of importance to solvent cleaning applications)	Residual coat of process liquid left after drainage; major problem in reactors and mixers in the paint manufacturing industry and generally in all high-viscosity liquid transfer operations.

The use of smooth heat exchanger surfaces results in lowering the adhesion of the deposit or its precursor to the surface. Application of electropolished stainless steel tubes in a forced circulation evaporator used in black liquor service in a paper mill resulted in a dramatic reduction of cleaning frequency from once a week to once a year 2/. Smooth non-stick surfaces can also be provided by Teflon (a registered trademark of E.I. Dupont de Nemours & Co.). Teflon heat exchanger designs are commercially available, as are designs utilizing Teflon coated steel. In a separate application, condensers using Teflon-coated tubes have been shown to drastically reduce fouling and resist corrosion while maintaining high thermal efficiency. The higher cost of material was weighed against reduced energy cost to show a 69 percent return on investment in the first year before tax 21/. If reduced cleaning costs were to be added, the ROI would have been higher.

The rate of heat exchanger fouling in a given service is dependent upon fluid velocity and, quite often, on film temperature. Film temperature controls the speed of chemical reactions which result in deposit-forming compounds while fluid velocity controls the shear rate at the fluid-deposit interface.

Hence, lowering the temperature of the heating medium and increasing the fluid velocity (e.g. by recirculation) can produce a desired reduction of the fouling rate. An economic trade-off analysis between the increase in pumping cost and the decrease in the cost of cleaning and other possible savings appears warranted in investigations relating the degree of oversizing to cleaning waste generation. A general review of thermal and hydrodynamic aspects of heat exchanger fouling was provided by Knudsen 3/.

Control of deposit precursors is often an obvious practical consideration. Proper maintenance of cooling water quality in open circulating systems is of paramount importance to water-side heat exchanger fouling. Control of hardness, pH, corrosivity and biofouling tendency is accomplished through careful monitoring of water quality 20/. In particular, biocides added in treatment must propagate the entire cooling fluid path in order to be deposited and function at all locations in the exchanger; and acid feed equipment to maintain the pH in the non-scaling range of 6 to 7 must be reliable or else rapid scaling or corrosion problems occur 3/.

The choice of heat exchanger type can influence cleaning frequency. For example, spiral plate exchangers are often specified over other designs in fermentation plants, owing to the ease of solid resuspension, absence of pockets, and non-plugging characteristics. Rod baffle design provides more effective shell-side turbulence at lower pressure drop compared to a more conventional segmented baffle design. Therefore, the rod baffle design can be expected to exhibit superior shell-side fouling characteristics.

Slowing down the rate of deposit formation is not limited to heat exchangers, but also is important for other types of equipment. For example, crude oil's exposure to atmospheric oxygen can cause formation of gums and resins during long exposure periods inside storage tanks. The use of floating roof tanks or inert gas blanketing has been suggested as a way to reduce tank deposit buildup 4/. Similarly, in paint manufacturing, exposure to air causes formation of solid films that adhere strongly to the internal surface of the mixers. This can be avoided by using closed storage and transfer systems, as evidenced by experience at Ford Motor Company. At Ford, the paint storage and transfer system was enclosed and redesigned for full recirculation resulting in less frequent and easier cleanups and an improvement of paint quality 5/. Other applications of fouling inhibition include coating of reactor internals with special chemicals to prevent scale formation. These practices have been used in the suspension polymerization process for polyvinyl chloride 6/.

Maximizing dedication of process equipment to a single process function or formulation will reduce cleaning frequency, as the frequency of switching to different formulations will diminish. Maximum dedication means either converting from a batch to a continuous process or using the equipment intermittently just for one formulation.

Historically, the changeover from batch or cyclic to continuous operations has been common in the chemical industry, owing to increased product demand, increased labor costs and technological progress. The advantages of the continuous process over batch include the ease of automation and control (which minimizes human error leading to inferior product quality) and lower labor requirements.

The choice between the continuous or batch mode is governed primarily by production volume and related trade-offs between capital and operating costs. The batch process is advantageous in situations where production volumes are small and product diversity large. Batch processes have proven advantageous even for certain large volume products, such as, neoprene rubber and phenolic resins, where continuous alternatives were developed but failed to find wide application [7,8].

Dedicating a piece of equipment to a single formulation in the batch process means that the equipment remains dormant between individual production campaigns. Cleaning after each campaign can be avoided provided that materials left in the equipment do not deteriorate with time or corrode the internals. Also, the cost penalties associated with equipment under-utilization must be outweighed by cleaning costs incurred when the equipment is used with more than one formulation.

Proper production scheduling is a commonly invoked method to decrease cleaning frequency. Equipment utilization strategies and the resulting production schedules should be derived through optimization analysis, where the objective is to meet the desired production goals with due consideration of such constraints as available equipment, cost of turnaround, labor availability, storage, etc. Meeting production goals is to be accomplished with minimum cost, which includes minimization of cleaning frequency. A general review of optimum strategy formulation was given by Peters and Timmerhaus [9].

However, in a typical situation a formal optimization analysis is not used often. Rather, a common-sense approach to production scheduling is used based on trial-and-error preparation of production bar-charts. To reduce cleaning waste, it is generally desirable to schedule long campaign runs, as opposed to short and more frequent runs. Production schedulers now must be aware of the current waste disposal costs, an aspect that previously could have been ignored.

Avoidance of unnecessary cleaning should be one of the goals of waste minimization audits. At times, equipment cleaning is performed routinely with little or no consideration of the rationale for the cleaning activity. An actual case is known where a ball mill was used periodically to wet-grind a certain powder. The ball mill with corrosion-proof internals was totally dedicated to the same formulation, a stable mixture of inorganic powders. Yet, the ball mill was cleaned after each use for no apparent reason. Upon questioning, the only justification provided was that the other non-dedicated ball mills at the facility were cleaned after every use.

REDUCTION OF QUANTITY AND TOXICITY OF CLEANUP WASTE

When cleaning has to be performed, it should be performed effectively with minimal generation of waste. Typical considerations include the choice of cleaning medium, cleaning technique and waste disposal option. A brief overview of these choices (with the exception of waste disposal), is provided in the following paragraphs.

A distinction can be made between chemical and mechanical cleaning. Chemical cleaning requires the use of substances such as those shown in Table 2 which are employed to chemically attack the deposits and render them either solvent or water-soluble. The basic reaction types include oxidation, reduction, chelation or conversion of insoluble oxides into soluble salts. Cleaning formulations also include surfactants to lower surface tension of solution to allow for faster penetration and breakup of deposits.

Physical or mechanical cleaning relies on breaking the adhesion of the deposit to a surface using mechanical devices, such as scrapers, squeegees, rags, drag lines, "pigs", lances or through the use of high velocity water jets (hydroblasting). Often mechanical and chemical cleaning are combined, e.g., when high velocity jets are employed with caustic solutions to attack deposits in paint mix tanks.

According to a classification developed by Loucks 10/, six separate cleaning techniques are distinguished:

- fill-and-empty technique
- circulation technique
- "flow over" technique
- gas propel technique
- process simulation technique
- onstream cleaning technique

In the "fill-and-empty" technique, a process vessel is isolated from other equipment and filled with an appropriate cleaning solution. The solution can be heated and agitated and, after a period of 4 to 8 hours it is drained. Rinse-water or diluted alkali or acid solutions are then used to remove residual cleaning chemical. Drained chemicals and subsequent rinses are either reused, treated, recycled or land-filled

TABLE 2. SOME CHEMICAL CLEANING COMPOUNDS AND THEIR USAGE

Cleaning Compound	Chemical Action	Usage	Remarks
Hydrochloric Acid	Dissolves most water scales and corrosion products	Used on boilers, heat exchangers, pipelines, etc.	Corrosive to steel; temperatures must be below 175°F
Sulfuric Acid	Dissolves most corrosion products	Limited use	Cannot remove water scales
Nitric Acid	Same as HCl	Used for stainless steel and aluminum	Cannot be used for copper and ferrous alloys
Hydrofluoric Acid	Dissolves silicate deposits	Used as an additive to HCl (as ammonium bifluoride)	Very dangerous to handle
Sulfamic Acid	Dissolves calcium salts	Used as an additive to HCl	Easy to handle; soluble calcium salts
Citric Acid	Dissolves iron oxides	Used mostly to clean boilers; frequently with added ammonia and oxidizers	Not good for water scale removal
Caustic Soda, Soda Ash	Dissolves oil and grease	Used to remove oil and grease before acid cleaning and to neutralize the acid after cleaning	Dangerous to handle
Ammonia	Forms soluble complexes with copper ions	Used to remove copper from large boilers	Needs to be handled carefully
Ethylene Diamine Tetra-Acetate (EDTA)	Dissolves water scales at alkaline pH's	Used for cleaning water systems without shutdown	Expensive

Source: References (10), (20).

depending on their composition and the availability of disposal options at the particular site. The method uses large quantities of chemicals and requires substantial downtime. It is typically applicable to small vessels, tanks or heat exchangers.

In the "circulation" technique, the vessel is filled with cleaning solution to an overflow and allowed to stand for a short time period, after which the solution is circulated with an auxiliary pump. Fresh make-up solution can be pumped in if used solution is withdrawn. In boilers, nitrogen gas is used to provide agitation for more effective scale removal.

The "flow over" technique consists of spraying the solution onto the surface. It is applicable to large tanks where cleaning by filling or recirculation would require excessive quantities of cleaning solution. Extra safety precautions are usually necessary.

The "gas propel" technique utilizes cleaning agents that are not overly corrosive at higher temperatures when steam is used to propel them through the system. This technique is useful for pipelines, where inhibited organic acids or chelants are entrained into a flow of steam which carries the liquid drops and solids debris through hydraulic obstacles of the system.

The "process simulation" technique is applied to equipment that is easily fouled and where spare parallel units are provided. Fouled equipment is cleaned by simulated process operation, where the equipment is isolated, drained of process fluid and filled with the cleaning solution using process pumps and controls to maintain flow and temperature. An example is removal of iron oxide and copper deposits from high pressure steam generators using ammoniated EDTA solution.

The "onstream cleaning" technique is probably the most preferable method, as it relies on process fluid to do the cleaning during normal operation. Often auxiliary mechanical devices are used along with additives, such as EDTA or acids to promote deposit removal. This technique is used for cleaning reactor jackets, gas compression station engines, heat exchangers, and other equipment. In-service cleaning of large circulating cooling water systems is often done through intermittent pH swing to the acid side of neutral and back again. Among many mechanical devices used in conjunction with onstream cleaning, one could mention ram valves for rodding out plugged nozzles and moveable heat exchanger tube inserts propelled by reversing process fluid [11]. In a separate example, the use of fluidized beds of inert solids (e.g., sand) was found useful in heat transfer applications characterized by extreme fouling, such as heat recovery from geothermal brines. Solid particles constantly abrade the deposit away from the heat transfer surface, maintaining high transfer rates.

The choice of cleaning method and media, apart from cost, should also be based on the following environmental considerations:

- minimize the amount of cleaning solution used;
- choose the medium ultimately resulting in the least toxic waste;
- determine ahead of time how the cleaning waste is going to be disposed of.

The use of chemical cleaning (e.g., with mineral or organic acids) results in appreciable quantities of hazardous cleaning wastes which need to be treated prior to disposal. As appropriate treatment facilities are not available onsite in every case, mechanical cleaning and onstream cleaning appear preferable to chemical cleaning. According to information obtained from various cleaning contractors, these factors are gaining recognition as the recent trend has been more toward hydroblasting and onstream cleaning and away from chemical cleaning. This was attributed to the rising costs of waste disposal and treatment.

When chemical cleaning is unavoidable, the least toxic medium should be chosen; for example, an alkaline cleaner would be preferable over a halogenated solvent. However, if the toxicity of the "soil" to be removed is the controlling factor, the cleaning agent with a higher potential for recovery and reuse should be used.

An attractive alternative to those cleaning methods that require disassembly of equipment for cleaning, is a clean-in-place (CIP) system. The system is composed of tanks, heat exchangers, filters, pumps, piping and instrumentation permanently installed as an auxiliary system designed to circulate a controlled inventory of cleaning solution through isolated process equipment often using spray manifolds or liquid jet nozzles inside production vessels. The CIP systems generally reduce the usage of cleaning medium. They are especially effective when coupled with high velocity automated jet manifolds and staged counter-current rinsing; an 80 to 90 percent reduction in aqueous waste was achieved by paint manufacturers after installing high pressure spray nozzles for tank rinsing 12/. CIP systems are popular in food, pharmaceutical and paint industries; however they are utilized less frequently in the chemical processing industry 13/.

Reuse of cleaning solutions is common in CIP systems. In general, reuse of cleaning solutions is highly desirable, especially if they can be utilized as part of formulation. For example, a considerable reduction in reactor cleanup waste was achieved by Borden Chemical where a two-step rinse sequence was applied to a batch kettle arrangement used for phenolic resin synthesis. The first rinse used a small amount of water generating a concentrated stream which could be recycled to the process. The second full volume rinse generated wastewater with a much lower content of toxic material than a previously used single rinse method 14/. Other examples include reuse of rinsewater from latex tank cleaning as part of latex formulation in the paint industry 15/ and use of warm oil for flushing the deposits out from crude oil storage tanks in an oil refinery, followed by solids separation in the slop oil system 16/.

The preceding sections were concerned with reduction of cleaning frequency and with the choice of the least waste-intensive cleaning methodology. There is a related, but independent aspect of cleaning waste reduction, i.e., reduction of clingage. As explained previously, clingage is the amount of process material left inside the vessel or other equipment after draining. In operations involving viscous fluids, such as paint manufacturing and resin compounding, clingage is an important consideration as it not only results in waste which is expensive to dispose of, but also represents a direct loss of product or raw material.

To reduce clingage, the following measures should be considered:

- provision of adequate drainage time;
- use of low-adherence surfaces, e.g., fluorocarbon or electropolished steel;
- use of mechanical wall wipers (dual shaft mixers);
- use of manual wipers or squeegees;
- choice of square cylindrical or spherical geometry to minimize wetted surface;
- rotation of agitator after batch dumping to reduce clingage on the blade.

All of the above measures are self-explanatory and do not require elaboration. Most are practiced extensively throughout industry. The use of tank linings as a means of reducing adherence and preventing corrosion has been addressed by Zolin [17] and Kays [18]. The use of dual shaft mixers with slow scraper blades wiping the walls and the bottom of mixing tanks is common in applications involving viscous liquids [19].

COST OF CLEANING

The cost of cleaning can be viewed as being composed of the following elements:

Direct Costs

- equipment assembly/disassembly
- cleaning chemicals and supplies
- waste treatment and disposal
- cleaning labor and supervision
- cleaning equipment depreciation
- utility costs

Indirect Costs

- planning and scheduling
- cost of lost production
- cost of lost raw materials inventory
- inspection and testing
- process equipment deterioration

Often equipment cleaning is performed by outside contractors with specialized equipment who assume the responsibility for hauling away the waste and for disposing of it properly.

Costs of cleaning vary widely depending upon the medium, method and application. Recent inquiries into the cost of cleaning of heat exchangers established the following compilation of relative heat exchanger cleaning costs using contracted service:

Method	Relative Cost
Hydroblasting	1.0
Rodding	4 to 5
Chemical Cleaning:	
Without waste disposal	0.3 to 3
With waste disposal	2.1 to 4

In many cases the cost of cleaning (taken as direct cost only) is lumped together with other maintenance costs. As a result, plant management may not have good visibility of the actual costs of cleaning, which may impede management's support for waste minimization efforts. Often, when plant management learns of the true cost dimension, action to lower cleaning costs is quickly initiated.

SUMMARY

As mentioned in the introduction, the intent of this paper is to provide a brief review of techniques, approaches and strategies for minimizing equipment cleaning waste and to provide a classification scheme that may serve as an initial guide to those interested in waste minimization. Such a classification or summary is provided in Table 3. This serves as a prototype checklist for addressing all waste minimization issues in a logical sequence.

The subject of equipment cleaning is quite diverse as the function is performed in virtually every industry. Generalizations presented in this paper must be translated into site-specific and exacting requirements in any waste minimization effort.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to the U.S. Environmental Protection Agency, Office of Solid Waste, for their support in developing a substantial portion of the material presented in this paper.

TABLE 3. WASTE MINIMIZATION OF EQUIPMENT CLEANING WASTE - SUMMARY OF APPROACHES

WHY IS DEPOSIT PRESENT?

REDUCE CLEANING FREQUENCY

1. Inhibition of fouling rate
    - smooth heat transfer surfaces
    - lower film temperature/higher turbulence
    - control of fouling precursors
    - choice of heat exchanger type
2. Maximize process equipment dedication
    - conversion from batch to continuous operation
    - dedication to single composition
3. Proper production scheduling
4. Avoidance of unnecessary cleaning

REDUCE QUANTITY AND TOXICITY OF WASTE

1. Minimize amount of cleaning solution
    - high pressure nozzles
    - flow-over technique
    - on-stream cleaning
    - use of CIP systems with staged or counter-current rinsing
    - reuse of cleaning solution
2. Minimize toxicity of spent cleaning solutions
    - clingage reduction
    - mechanical (hydroblasting) over chemical cleaning

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United States
Environmental Protection
Agency

Office of Research and
Development
Washington DC 20460

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Guide to Cleaner Technologies

Alternatives to Chlorinated Solvents for Cleaning and Degreasing

Available Technologies for Alternatives to Chlorinated Solvents for Cleaning and Degreasing: Descriptive Aspects and Operational Aspects

Table 2. Available Technologies for Alternatives to Chlorinated Solvents for Cleaning and Degreasing: Descriptive Aspects

Technology Type	Pollution Prevention Benefits	Reported Application	Operational Benefits	Limitations
Aqueous Cleaners	• No ozone depletion potential • May not contain VOCs • Many cleaners reported to be biodegradable	• Excellent for removing inorganic and polar organic contaminants • Used to remove light oils and residues left by other cleaning processes • Used to remove heavy oils, greases, and waxes at elevated temperatures (>160°F)	• Remove particulates and films • Cleaner performance changes with concentration and temperature, so process can be tailored to individual needs • Cavitate using ultrasonics	• Nonflammable and nonexplosive; relatively low health risks compared to solvents; consult Material Safety Data Sheet (MSDS) for individual cleaner • Contaminant and/or spent cleaner may be difficult to remove from blind holes and crevices • May require more floor space, especially if multi-stage cleaning is performed in line • Often used at high temperatures (120 to 200°F) • Metal may corrode if part not dried quickly; rust inhibitor may be used with cleaner and rinsewater • Stress corrosion cracking can occur in some polymers
Semi-Aqueous Cleaners	• Some have low vapor pressure and so have low VOC emissions • Terpenes work well at low temperatures, so less heat energy is required • Some types of cleaners allow used solvent to be separated from the aqueous rinse for separate recycling or disposal	• High solvency gives cleaners good ability for removing heavy grease, waxes, and tar • Most semi-aqueous cleaners can be used favorably with metals and most polymers • NMP used as a solvent in paint removers and in cleaners and degreasers	• Rust inhibitors can be included in semi-aqueous formulations • Nonalkaline pH; prevents etching of metals • Low surface tension allows semi-aqueous cleaners to penetrate small spaces • Glycol ethers are very polar solvents that can remove polar and nonpolar contaminants • NMP used when a water-miscible solvent is desired • Esters have good solvent properties for many contaminants and are soluble in most organic compounds	• NMP is a reproductive toxin that is transmitted dermally; handling requires protective gloves • Glycol ethers have been found to increase the rate of miscarriage • Mists of concentrated cleaners (especially terpenes) are highly flammable; hazard is overcome by process design or by using as water emulsions • Limonene-based terpenes emit a strong citrus odor that may be objectionable • Some semi-aqueous cleaners can cause swelling and cracking of polymers and elastomers • Some esters evaporate too slowly to be used without including a rinse and/or dry process • May be aquatic toxins
Petroleum Hydrocarbons	• Produce no wastewater • Recyclable by distillation • High grades have low odor and aromatic hydrocarbon content (low toxicity) • High grades have reduced evaporative loss	• Used in applications where water contact with parts is undesirable • Used on hard-to-clean organic contaminants, including heavy oil and grease, tar, and waxes • Low grades used in automobile repair and related service shops	• No water used, so there is less potential for corrosion of metal parts • Compatible with plastics, most metals, and some elastomers • Low liquid surface tension permits cleaning in small spaces	• Flammable or combustible, some have very low flash points, so process equipment must be designed to mitigate explosion dangers • Slower drying times than chlorinated solvents • The cost of vapor recovery, if implemented, is relatively high
Hydrochlorofluorocarbons (HCFCs)	• Lower emissions of ozone-depleting substances than CFCs • Produce no wastewater	• Used as near drop-in replacements for CFC-113 vapor degreasing • Compatible with most metals and ceramics, and with many polymers • Azeotropes with alcohol used in electronics cleaning	• Short-term solution to choosing an alternative solvent that permits use of existing equipment • No flash point	• Have some ozone depletion potential and global warming potential • Incompatible with acrylic, styrene, and ABS plastic • Users must petition EPA for purchase, per Section 612 of CAAA

(continued)

Table 2. (Continued)

Technology Type	Pollution Prevention Benefits	Reported Application	Operational Benefits	Limitations
Miscellaneous Organic Solvents	• Do not contain halogens, so they do not contribute to ozone depletion • Most are considered biodegradable • Generate no wastewater when used undiluted	• Most are used in small batch operations for spot cleaning	• Alcohols are polar solvents and are good for removing a wide range of inorganic and organic contaminants; soluble in water and may be used to accelerate drying • Ketones have good solvent properties for many polymers and adhesives; they are soluble in water and may be useful for certain rapid drying operations • Vegetable oils are used to remove printing inks and are compatible with most elastomers • Lighter alcohols and ketones have high evaporation rates and therefore dry quickly	• Most evaporate readily and therefore contribute to smog • Alcohols and ketones have low flash points and present a fire hazard • Inhalation of these solvents can present a health hazard • Some have vapor pressures that are too high to be used in standard process equipment • MEK and MIBK are on EPA list of 17 substances targeted for use reduction
Supercritical Fluids (SCFs)	• Nonpolluting when CO_2 is used as the supercritical fluid • Generate no wastewater • Use natural or industrial sources of CO_2, so no net production of carbon	• Remove organic contaminants of moderate molecular weight and low polarity • Precision clean instrument bearings, electromechanical assemblies, direct access storage devices, optical components, polymeric containers, porous metals, ceramics • Low viscosity and high diffusivity permit cleaning in very small cracks and pore spaces	• Compatible with metals, ceramics, and polymers such as Teflon™, high-density polyethylene, epoxies, and polyimides • No solvent residue left on parts • May be very useful for cleaning oxygen equipment • Solvent properties can be altered by adding a cosolvent	• Cosolvents used to improve the solvent power of CO_2 may have a pollution potential • Danger of a pressure vessel explosion or line rupture • Cause swelling in acrylates, styrene polymers, neoprene, polycarbonate, and urethanes • Components sensitive to high pressures and moderate temperatures should not be cleaned by SCF methods • Ineffective in removing inorganic and polar organic contaminants; for example, does not remove fingerprints
Carbon Dioxide Snow	• No polluting emissions released • Replaces CFCs and solvents • Does not generate wastewater • Uses natural or industrial sources of CO_2, so no net production of CO_2 occurs • Carries contaminants away in a stream of inert CO_2	• Cleans critical surfaces on delicate fiber optic equipment • Cleans radioactive-contaminated components • Used in hybrid circuits to remove submicron particles • Used on the largest, most expensive telescopes • Removes submicron particles and light oils from precision assemblies • Removes light fingerprints from silicon wafers and mirrors • Prepares surfaces for surface analysis	• Generates no media waste, thus no media disposal cost • Does not create thermal shock • Is nonflammable and nontoxic • Noncorrosive • Leaves no detectable residue • Can penetrate narrow spaces and nonturbulent areas to dislodge contaminants • Adjustable flake size and intensity • More effective than nitrogen or air blasting • Can clean hybrid circuits without disturbing the bonding wire	• CO_2 must be purified • Requires avoidance of long dwell times • Particulates such as sand may be carried by the gas stream and scratch the surface • Heavier oils may require the addition of chemicals and heat to be completely removed

Table 3. Available Technologies for Alternatives to Chlorinated Solvents for Cleaning and Degreasing: Operational Aspects

Technology Type	Process Complexity	Required Skill Level	Waste Products and Emissions	Cleaner Cost per Gallon	Energy Use	Optional Post-Cleaning Operations	References
Aqueous Cleaners	Medium	Medium	• Skimmed oil; filter-trapped particulates and greases; wastewater and detergent	$6-10; typical dilutions range from 1:3 to 1:9	Medium—temperature control, mechanical control, drying	• Rinsing—Some cleaners may leave a residue; to facilitate removal use DI water and/or alcohol • Drying—May be accelerated by blowing with hot air or rubbing with absorbent material; automated dryers are available	Gavaskar et al., 1992 Monroe et al., 1993 Munie, 1991 Murphy, 1991 Polhamus, 1991 Ross and Morrison, 1988 U.S. EPA, 1991a, b, c Weltman and Evanoff, 1992
Semi-Aqueous Cleaners	Medium	Medium	• Waste terpene containing mostly organic material and aqueous part containing mostly inorganic material; filters trap particulates, grease, and non-emulsified oil	$10-20; typical dilutions range from none to 1:9	Low—mechanical control, drying	• Cleaners may leave residue that is slow to evaporate; water rinse may be required • Drying may be needed if a water rinse is used; rinsing with alcohol will speed drying	Darnall et al., 1976 Hill and Carter, 1993 IPC, 1990 National Toxicology Program, 1990 U.S. EPA, 1991a, b, c U.S. EPA, 1993
Petroleum Hydrocarbons	Low	Medium	• Produce no wastewater when used undiluted. VOCs are emitted; waste solvent incinerated as fuel or recycled by distillation	$1-3 for kerosene and mineral spirits; $7-12 for metal cleaning formulations; up to $30 for some specialty and electronic cleaning formulations; most often used without water	Low—mechanical control, drying	• Parts may be dried by forced air or by some other method	IPC, 1990 U.S. EPA, 1991a, b
Hydrochloro fluorocarbons (HCFCs)	Low	Medium	• Still bottoms; contaminated solvent; HCFCs emitted to air unless closed-loop system is used	$30-35	High—maintain boiling temperature; run primary and possibly secondary condensing systems	• None	Basu et al., 1991 Finegan and Rusch, 1993 Kitamura et al., 1991 U.S. EPA, 1991a, b

(continued)

Table 3. (Continued)

Technology Type	Process Complexity	Required Skill Level	Waste Products and Emissions	Cleaner Cost per Gallon	Energy Use	Optional Post-Cleaning Operations	References
Miscellaneous Organic Solvents	Low	Low	• Waste solvents	$2-20	Low—primarily suited for small scale and local cleaning	• Vegetable oil cleaning requires a secondary cleaning step	Burow, 1993 Environmental Program Office, 1991 Hill and Carter, 1993 U.S. EPA, 1991a, b
Supercritical Fluids	High	High	• Contaminants are condensed in a vessel • CO_2 gas may be vented to the atmosphere or purified and reused	Cost of high-purity CO_2 (about 7¢/lb) is insignificant compared to installation cost	Low—Energy is required to operate pumps to perform supercritical cleaning	• Remove part from pressure vessel	Airco Gases, N.D. Gallagher and Krukonis, 1991 Lira, 1988 Salerno, 1990 Schneider, 1978 U.S. EPA, 1991 Woodwell, 1993
Carbon Dioxide Snow	Medium	Medium	• Solid coating residue waste • Airborne particulates • CO_2 gas	Cost of welding grade CO_2 is about 7¢/lb	Medium— • Carbon dioxide liquefier • Refrigeration unit • Compressed gas supply to propel blasting media • Requires current between 8 and 14.5 amps • Requires voltage between 115 and 230 V	• Requires dry air stream or chamber to prevent water condensation while parts are cold	Hoenig, 1990 Layden and Wadlow, 1990 Sherman and Whitlock, 1990 Whitlock, 1989 Zito, 1990

KNOW YOUR CLEANING ALTERNATIVES

Note: The following glossary of cleaning alternatives is provided for reference and definitive purposes only and is not intended as a promotion of any specific chemistry, product or technology.

ALCOHOL BASED CLEANING (AL)

These alternatives have found use in the electronics industry as CFC alternatives and areas requiring high degrees of cleanliness. Limitations to use are explosive risks, toxicity and emissions concerns. Benefits are quick parts drying time and low residuals.

Examples of alcohols used include: ethanol, methanol, isopropanol, and glycol.

AQUEOUS BASED CHEMISTRIES (AQ)

A.k.a. Water Based Chemistries, these fall largely into the alkaline, and acid families with other groupings containing surfactants, emulsifiers and detergents. Changing over to a water based cleaning operation will of course result in some increase in water discharge. Many technologies exist to separate the water from the spent cleaners for reuse in make-up of new chemical baths. Drying time of parts may increase and therefore problematic for work that tends to rust quickly.

HYDROCARBON BLENDS(HB)

Hydrocarbon blends seek to fill the market of drop-in alternatives to chlorinated solvents and CFCs. Many offer a quick changeover using existing tanks and equipment. Caution should be exercised is choosing a blend to make sure the components are not scheduled to be phased out or banned. Many blends have excellent cleaning abilities with some reduced risk to workers. The SARA Title III list should be consulted to determine if the chemical is regulated.

NON-AQUEOUS CHEMISTRIES (NA)

This category distinguishes these alternatives from their water based counterparts, though many of these alternatives have water as a component. They often clean more aggressively than their water based counterparts. The toxicity of some of these alternatives has not been completely determined. Some are listed under the SARA Title III reporting.

NON-LIQUID ALTERNATIVES (NL)

This category covers all types of solid stripping media such as CO2 pellets, plastic blast media, sponge pellets, and dry ice flakes, Also included are super critical fluids alternatives. The blast media are excellent for cleaning large parts and simple geometries. Delicate instruments and blind holes are not well suited to these applications. Super critical CO2 has been used successfully on small to medium sized applications. Capital costs for installing the pumps and high pressure vessels has prohibited it's wide-spread usage.

TERPENE / SEMI AQUEOUS CHEMISTRIES (TP)

Terpenes have found a wide variety of uses in the electronics industry and cleaning parts with complex geometries. They are often coupled with ultrasonic or similar agitation devices. The long term toxicity of terpenes and other pine and citrus derivatives remains a matter of

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Anonymous. *1994. Know Your Cleaning Alternatives.* The Catalyst 1(2):4-5. Reproduced with permission from the New Jersey Technical Assistance Program, Newark, New Jersey.

study. Early varieties tended to have low flash points; a problem that has been well addressed by today's chemical vendors.

Examples of terpene include d-limonene, a terpineol derivative extracted from citrus fruit.

CIRCUIT BOARD CLEANING SYSTEMS (BC)

This category is important to high tech industries. Vendors sell these chemistries as low solid fluxes and no-clean fluxes.

CUSTOM DESIGNED SYSTEMS (DS)

These are large conveyorized or monorail cleaning systems. The entire system can be tailored to the facilities work centers and parts flow. Because of the substantial cost, a thorough survey of cleaning practices that establishes that there is a need to clean is urged. Process and chemical modifications may reduce or eliminate the need for cleaning, thereby saving capital.

IMMERSION TANKS (IT)

Immersion tanks come in a wide range of sizes and are often coupled with agitation or ultrasonics, which reduces the need for a highly aggressive solvent that might damage the work.

ROTARY PARTS WASHERS (RW)

These systems are designed to function similar to large washing machines and dish washers. Most are of the cabinet variety with a turntable in the center to spin the parts as cleaning jets direct the solvent onto the parts or baskets of parts. Rotary washers can also help dry parts by spinning the liquid off or blowing it off with compressed air.

SPRAY WASH SYSTEMS (SW)

Very similar to Rotary Washers, these may even contain a rotating basket within an immersion tank. Spray wash systems work by agitating parts and forcing solvents into blind holes and difficult geometries. They may not be useful for delicate instrumentation or sealed components where sprays might damage the parts.

ULTRASONICS (US)

Ultrasonic cleaning systems work through generating high frequency vibrations which cause the detergents to actively collide with the parts and soils. This impaction lifts the dirt and carries it away from the parts. Ultrasonic systems work well in most applications with two exceptions; part orientation with respect to the ultrasonic generating unit may cause shadowing, or zones of less aggressive cleaning; and electricity cost will be increased proportional to use. Therefore, large scale application may result in a significant increase in power demand.

Fact Sheet

ENVIRONMENTAL SERVICES DIVISION

State of Michigan • Departments of Commerce and Natural Resources

AQUEOUS AND SEMI-AQUEOUS CLEANERS

INTRODUCTION

The traditional way to clean an oily part was to dip it in a solvent or suspend it in solvent vapors. It was fast and effective. Today, however, the liabilities associated with worker safety and management of hazardous wastes and restrictions on production of some chlorinated solvents are motivating businesses to find alternatives to solvents in their cleaning processes. Aqueous and semi-aqueous cleaners are being advertised by their manufacturers as reliable substitutes for solvents in many different cleaning applications. Businesses have many questions regarding these substitutes. Are they effective in cleaning? What waste streams do they produce and how are they treated? Are they friendly to the environment and workers that use them? The purpose of this fact sheet is to help in determining if these cleaners can meet the needs and expectations of your particular requirements.

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FAX: (517) 335-4729

SMALL BUSINESS CLEAN AIR ASSISTANCE

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IDENTIFY THE NEEDS OF YOUR CLEANING SYSTEM

Switching cleaners is not as easy as it may sound. There are many variables that affect cleaning. Before evaluating alternative cleaners, assess the cleaning process needs. A check list of factors that affect the selection of a cleaner and its method of application follows.

What Types of Soil are to be Removed?

The first step in assessing cleaning needs is to identify the soils that need removal. The composition of soils to be removed is an important variable in cleaner formulation. If the manufacturing process and storage and handling conditions of the part are known, the type of soil that the part has been exposed to can be predicted. For example, if the parts have gone through machining operations, oils and greases used for lubrication, cutting, quenching and rust prevention must be removed. Consider the removal of solder flux residues when cleaning electronic components. Parts exiting metal polishing and buffing operations are contaminated with waxes and abrasives.

As can be seen in Table 1, there are a variety of soils. Physical properties of soil include its state (liquid or solid), viscosity, polarity and melting point. Solid particles (metal chips, abrasive grains, pigments, carbon smut and shop dirt) are usually held on the part by oils and greases or static electricity. Because of the large surface area of the tiny particles, they hold on to the part with great tenacity. Liquid soils, such as lubricants and oils, which are left on parts for a long time or heated, can polymerize to form tough hard films. Also, soils with high viscosity and melting points are generally more difficult to remove.

The polarity of soils will affect the type of cleaner selected. Polar or ionic soils are positively or negatively charged particles due to the loss or gain of electrons. Most inorganic soils (substances that are not compounds of carbon) are polar, whereas most organic soils (substances that are compounds of carbon) are non-polar. Water is a polar substance. Most hydrocarbon liquids, with the exception of alcohols, are non-polar. The importance of polarity of both the soil and the cleaner will be addressed later, in the discussion of the cleaning mechanism of solvency.

Substrate

Zinc and aluminum alloys, because of their sensitivity to alkaline cleaners--which are corrosive--will require different cleaners than ferrous alloys. Aqueous cleaners for nonferrous alloys will be formulated with

TABLE 1

SOILS	
SOIL TYPE	**OPERATIONS**
Oily soils: animal, vegetable and petroleum oils	Metal cutting, metal forming and rust protection.
Semi-solid soils: greases, soaps, abrasives and waxes	Buffing and polishing
Solid soils: carbonaceous films, metal oxides and shop dirt	Heat treating and storage

inhibitors that prevent the alkalies from attacking the sensitive metals. The inhibitors deposit a thin protective layer on the metals as soon as the contaminants are removed. The majority of aqueous and semi-aqueous cleaners are compatible with most metals and plastics.

Part Size and Configuration

Part configuration, size, weight, porosity, and quantity will not influence cleaner chemistry, but will determine the method of cleaning and parts handling. Parts with rough surfaces, overlapping joints, blind holes and tubing must be positioned to avoid corrosion from the carry out of cleaner. Very large castings may affect temperature of the cleaning bath and more heat must be added to the cleaning bath to maintain cleaning efficiencies.

What is the Acceptable Level of Cleanliness?

The level of cleanliness is dependent upon performance requirements of the part. Parts going on to a painting or electroplating process will have to be "cleaner" than if the parts were headed to a machining operation. Many standard tests can be used to determine if the acceptable level of cleanliness is being met. They range from visual inspection to elaborate laboratory testing. A simple and reliable procedure is the water-break test. A surface is considered clean if it can hold a complete film of water on the surface of the work after a 30 second drainage period. If a water-break appears, the surface is not clean.

Other Considerations

Source Reduction: One way of reducing costs and increasing the potential of making a successful conversion to a new cleaning system is to reduce the amount of contamination on the parts. Once the source of the contaminants is identified, modifications can be made that will reduce or eliminate the need for cleaning. If the soils are:

- received in raw materials, talk to suppliers about what they can do to reduce the contamination;
- produced in general machining operations, minimize the number of different coolants and/or lubricants used;
- produced in subassembly, find ways to reduce handling; or
- produced during storage, reduce moisture.

Potential Impacts: In order to successfully make the switch to your new cleaning system and reduce the impact to other operations, consider the following questions:

> *What are the waste streams that will be created by the new system and how are they to be managed?*
>
> *What new operating skills or equipment maintenance will be needed? Process controls for aqueous and semi-aqueous cleaning systems are greater than those needed for solvent cleaning systems.*
>
> *How will the modification affect product quality and operating rates?*
>
> *What are the capital and operating costs? Energy requirements for aqueous cleaning systems are greater than solvent vapor degreasing.*
>
> *And finally, have any substitutions been attempted in the past? What worked? What did not work and why?*

EVALUATION OF AQUEOUS AND SEMI-AQUEOUS CLEANERS

Cleaning Step

Unlike solvent cleaning, which occurs in one step, aqueous and semi-aqueous cleaning involves three steps: cleaning, rinsing and drying. The cleaning phase in aqueous and semi-aqueous systems differ; however, the rinsing and drying steps for aqueous and semi-aqueous cleaning systems are nearly identical.

Cleaning Mechanisms

A discussion of aqueous and semi-aqueous cleaning should not proceed without some understanding of the following four basic cleaning mechanisms:

Mechanical action - This is the lifting of contaminants by physical agitation, i.e., wiping, brushing, spraying or abrading.

Chemical reaction - There are two basic chemical reactions that can occur in aqueous cleaning: saponification and sequestration. Saponification occurs when the alkalinity of the aqueous cleaner "splits up" fatty acids, a contaminant, to form water soluble soaps that can be easily removed. Sequestering agents (polyphosphate salts of sodium) or chelating agents (ethylenediamine tetracetic acid) are added to cleaner formulations to "tie-up" or sequester the calcium and magnesium ions in hard water so that they do not interfere with cleaning. The hard water ions are formed into ringed structures that are water soluble and chemically inactive. If not sequestered, the ions will react with soap to form scum.

Solvency - Soils (or solutes) will dissolve in a solvent forming a uniformly dispersed mixture or solution. Water, being a polar substance, is the solvent for many polar (or ionic) soils. Hydrocarbons, being non-polar, are the solvents for non-polar or organic soils. Solubility is the term commonly used to describe the ability of solids to dissolve in

SURFACTANTS

Surfactants, also known as surface-active agents, are composed of molecules that have two dissimilar parts resembling a tadpole. The tail end is made up of a chain of carbon atoms and is soluble in oil or, in other words, attracted to dirt, oil and grease. The head is ionic and is attracted to water. The nonpolar hydrocarbon end stays in the oil and the polar, ionic end is in the water. Because of this antagonistic action, surfactants like to concentrate at surfaces or interfaces.

As the number of carbon atoms included in the chains increase, the surfactant molecules' oil attractive properties increase and their water attractive properties diminish. Surfactants with relatively high oil-attractive properties are called **emulsifiers.** Emulsifiers coat oil and grease, which forms an emulsion. The emulsifiers suspend the organic soils and grease and other water immiscible soils in solution and prevent redeposition. Surfactants with relatively low oil-attractive properties are called **wetting agents.** Wetting agents increase the penetration of the cleaner on the surface or soil by reducing surface tension. **Detergents** possess oil-attractive properties between those of wetting agents and emulsifiers. Detergents lift soil from the surface of the part by replacing it with a surfactant, which has a greater affinity for the soil.

Detergents or synthetic surfactants are made from alcohols or petroleum derived fractions. Soap is an organic surfactant formed by the reaction of fatty acids (derived from natural fats, such as tallow, fish oil and vegetable oils) and caustic soda.

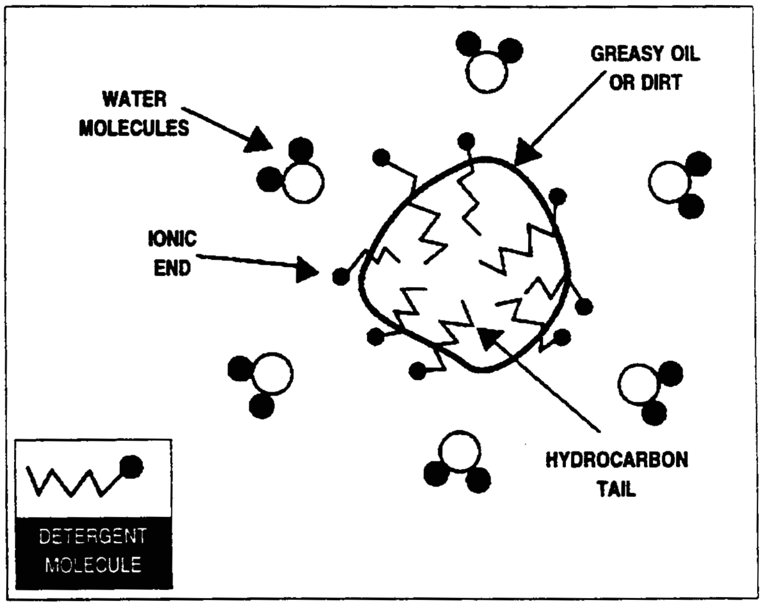


Illustration of an emulsified drop of oil in water with detergent as the emulsifier. The nonpolar hydrocarbon tail of the detergent molecule is in the oil, and the ionic end is in the water.

liquids and miscibility is the ability of a liquid to dissolve in another liquid.

Detergency - This is the lifting of soil from a surface by displacing it with surfactants that have a greater affinity for the soil than the surface. The surfactants also provide for the dispersion of the contaminates, which is necessary to prevent recontamination.

Aqueous Cleaners

•*How Do They Work?*

Aqueous cleaners are categorized by pH level. Cleaners with a low pH (2 to 6) are acidic and those with a pH of 6 to 8.5 are considered neutral. Cleaners that have a high pH (8.5 to 13) are considered basic or alkaline. Acidic cleaners contain excess hydrogen ions (H+) and alkaline cleaners contain excess hydroxide ions (OH-). Acid cleaners are primarily used in removing oxidation scale and rust. Acid cleaners contain mineral acids (nitric, phosphoric, sulfuric, and hydrofluoric); chromic acid or organic acids (acetic and oxalic); plus chelating agents, detergents and small amounts of water-miscible agents.

Aqueous cleaners, because they are water based, are most effective on polar, inorganic based soils; however, a variety of additives enhance the cleaners to provide for the removal of organic soils as well. In aqueous cleaning, a combination of the cleaning mechanisms are employed: mechanical action, chemical action and detergency.

Because their performance can be affected by concentration, temperature and formulation, aqueous cleaners can be used in a variety of applications. Alkaline cleaners are formulated to be either broad spectrum or precisely applicable. Broad spectrum cleaners remove a variety of soils while precisely applicable cleaners are highly effective for a specific soil and not effective for many other soils.

•*Composition*

Aqueous cleaners contain several chemical components each having a distinct function and effect on the way soil is removed.

Alkaline Salts - Alkaline salts or alkalinity builders are the major components in alkaline cleaners. They act as buffers that neutralize acidic soils without excess loss of alkalinity and maintain the chemical environment in which other components of the cleaner operate.

Alkaline salts can be categorized by the way they condition or soften water. The two groups of alkaline salts are precipitating and sequestering. Precipitating salts will combine with hard water minerals making them insoluble. Sequestering salts will tie up minerals and soils and hold them in suspension, making them soluble. Examples of some common cleaners are found in Table 2.

TABLE 2

TYPICAL ALKALINE CLEANERS

PRECIPITATING TYPE	SEQUESTERING TYPE
Caustic soda (pH 14.0)	Sodium tripolyphosphate (pH 10.5)
Soda ash (pH 11.5)	Tetrasodium pyrophosphosphate (pH 10.0)
Trisodium phosphate (pH 12.0)	Sodium hexametaphosphate (pH 8.0)
Sodium metasilicate (pH 12.5)	
Sodium orthosilicate (pH 13.5)	

Footnote: *Scislowski, Stan "Cleaning Basics: Alkaline Cleaners" Metal Finishing.*

Sequestering type alkaline cleaners are more effective in preventing the buildup of hard water scale on tanks and pumps. They are effective in "peptizing" or holding soils in suspension, which prevents them from redepositing on the part. Phosphates are the best overall builders, however, their discharge is subject to regulation.

Precipitating alkaline cleaners have higher alkalinity and, therefore, higher pH. Silicates are used in cleaning non-ferrous metals such as zinc, brass and aluminum because they inhibit the corrosive action of the alkalinity. One disadvantage in using the precipitating type cleaners is their poor rinsibility. Hard water minerals that precipitate out cling to the sides and bottom of the tank. This contributes to the redeposition of soil onto the part.

Surfactants - Surfactants can penetrate, displace and/or emulsify soil. (See Page 4). They are classified as anionic, cationic or non-ionic. Anionic and cationic surfactants are used in immersion cleaning. A non-ionic surfactant should be used if aqueous spray cleaning or agitation is used in order to minimize foaming. Some of the commonly used anionic surfactants are alkyl benzene sulfonates and naphthalene sulfonates. Most surfactants are biodegradable. Soaps (organic surfactants) are destroyed in acid and perform better in alkaline conditions. The optimum alkalinity for soaps is 10.5.

Saponifiers - Saponifiers are alkaline cleaners that react chemically with insoluble animal fats and vegetable oils to form water soluble soaps. Saponified soils float to the top of the tank and are removed by skimming. Many buffing compounds contain insoluble fats and fatty acids.

Rustproofing Inhibitors - Compounds such as urea type inhibitors are added to the cleaners or used in the final rinse water to protect the part from rusting.

•*Methods of Application*

The cleaning phase in an aqueous cleaning system occurs in one step. The contaminants are removed from the parts in the tank containing the cleaner. The parts leaving the cleaning tank are coated with a water/detergent film containing minor amounts of contaminants. Cleaning cycle times for aqueous cleaning in industrial applications range from 2 to 30 minutes.

The method of cleaning is dependent on production rates, available space, and size and shape of part. The basic cleaning methods are immersion (dipping or soaking) with or without agitation, spraying or by a combination of immersion and spraying. The different types of cleaning machines are found in Table 3.

Immersion - Immersion of parts into a cleaning tank is simple, efficient and is the most widely practiced aqueous cleaning method. Tanks can accommodate parts of unusual shape and are not costly to set up.

Installations may vary from single unheated tanks to multistage systems equipped with heat and agitation. Aqueous cleaners need to be heated, especially when removing inks, waxes or solder pastes. The normal temperature of the cleaner is in the range of 160°-200° F. The speed of chemical reactions in cleaning doubles with each 20° F rise in temperature. Heat is provided by steam coils, plate coils, direct firing burners or immersion electric heaters. Low temperature cleaners, which operate at a temperature range of 70° - 120° F, are a little more expensive to purchase; however, they can greatly reduce energy costs and still provide good cleaning.

Workpieces and/or cleaning solution are agitated to improve cleaning efficiency and reduce cycle times, temperature requirements and the formation of air pockets. Agitation for immersion cleaning includes workpiece movement, such as withdrawal and reimmersion, pump agitation and ultrasonics.

TABLE 3

TYPES OF CLEANING EQUIPMENT		
MACHINE	**VOLUME OF PARTS**	**TYPE OF PARTS**
Flat belt	Medium-High	Parts that drain easily
Rotary drum	Medium-High	Small intricate parts and irregular shapes that trap fluids
Monorail	Low-High	Large sheets
Turntable	Low	Parts requiring special positioning for draining
Cabinet	Low	Medium to large sized parts of any shape

Pumps should be used for solution agitation rather than blowers or compressors. Providing agitation through air pressure movement can introduce contaminants into the cleaning bath and can create excessive foaming. Ultrasonics create cavitation (bubbles) at the cleaning surface using high frequency vibrations. As the bubbles form and collapse, they create a scrubbing action that cleans the surfaces of the part including blind holes and very small cracks and crevices.

Quite often, existing equipment such as vapor degreasers can be converted to the use of aqueous cleaners. Under the direction of some manufacturers of aqueous products, the changes can be implemented quite easily and economically.

Spray Cleaning - Spray cleaning involves the impingement of cleaning solution upon the workpiece to remove soil. It is typically used for conveyorized part handling systems and high production rates. Spray washers consist of a pump to pressurize the solution, a reservoir tank, connecting piping, spray nozzles and a means for moving workpieces through the nozzles and cleaning solution.

For small parts, cabinet or carousel machines provide the simplest method of spray cleaning. Inside the machines, a drum or worktable rotates or reciprocates so that surfaces of all the workpieces can be exposed to the spray.

Large flat parts are typically carried through washer tunnels or monorail washers by conveyor.

The spraying action provides a high level of impact and agitation. Spray pattern, volume, pressure and angle of spray can have an effect on cleaning efficiency. The higher the spray pressure, the greater the mechanical cleaning action. Spray pressure can vary from 2 to 2000 psi. The design of the spray nozzle is critical because it provides the high impact, flat spray pattern and required flow rates. Increasing the spraying pressure results in higher impact velocities and flow rates with smaller drop sizes.

While it is difficult to maintain the cleaner at a high temperature because of heat loss during recirculation and spraying, it is still desirable to keep the cleaner in the temperature range of 130°-160° F. Cleaners used in spray washers require non-ionic surfactants to prevent foaming.

Spray cleaning has some advantages over immersion in that it takes less time to clean and a lower concentration of cleaner is used. The amount of cleaner can be as low as 10% of that required for immersion cleaning. One disadvantage, however, is that the capital costs for spray cleaning is greater than for immersion cleaning.

•Safety

Aqueous cleaners are nonflammable. Because of their alkalinity, aqueous cleaners have an ability to extract oils out of skin. Workers should wear rubber gloves, aprons and face shields to prevent contact with skin. Handling and safety requirements identified in the cleaner's Material Safety Data Sheet (MSDS) should be followed without exception.

•Cost

Aqueous cleaners are available in concentrated liquids and powders. Liquids cost $6 to $10 per gallon when purchased in drum quantities. In most applications, the cleaner is diluted with water within the following range; 1 part cleaner to 3 parts water (1:3) to 1 part cleaner to 10 parts water (1:10). In an effort to reduce waste disposal costs, some manufacturers are packaging liquid cleaners in recyclable 250 gallon containers.

•Recovery and Disposal

Recovery - In parts cleaning systems, cleaning power and contamination level are inversely proportional. By continually removing contaminants from the cleaner, the cleaning ability is maintained and thus the cleaner can be recycled indefinitely.

Increasing the longevity of the cleaner starts with selecting the proper cleaner formulation. Purchase a cleaner that provides good separation of the soils from the cleaner. New oil-displacing cleaners, or cleaners that are good detergents but poor emulsifiers, allow the separation to occur. These cleaners will allow oily soils and saponified soils to float to the surface where they can be skimmed off. The heavy soils settle to the bottom where they can be filtered off and collected as a sludge.

Cleaners containing emulsifiers can form one of two types of emulsions: permanent or quick breaking. Permanent emulsions keep the oil in suspension indefinitely, and quick break emulsions are temperature sensitive, which allows rapid separation of the water and organic contaminant.

In cleaners containing quick break emulsions, oils are put into suspension at operating temperatures of 140° F and above. Upon cooling to 85° F, the oil will separate from the water and cleaning component mixture, forming two layers. The organic oil layer can be disposed and the water/cleaning component layer can be reused. Cleaners with quick break emulsifiers cost more but have a longer life.

In addition to choosing the right cleaner, there are various processes that can remove contaminants so that the cleaner and rinse waters can be can be continuously recirculated. Free oils, emulsified oils, and suspended soils and metals are the contaminants that should be removed continuously or periodically from the aqueous cleaner bath and rinse water.

A continuous small stream of cleaner can be directed to a concentration or clarifier tank located adjacent to the cleaning bath tank (see Figure 1 on page 9). The concentration tank provides for the separation of solids and liquids by gravity and floatation. The free oils that float to the top of the tank can be removed by oil skimming devices or absorbent mats that pick up petroleum based fluids but repel water and product. The contaminants heavy enough to settle out can be passed through a bag filter or filter press and removed as a sludge.

Microfiltration membranes, which have a pore size of greater than 0.2 microns, remove dirt and contaminants (concentrate) from the cleaner bath while allowing the cleaner and water (permeate) to pass on through. The cleaner and water are returned to the cleaning bath tank. Ultrafiltration membranes, which have a pore size between 0.001 and 0.1 microns, can also remove contaminants from the rinse water.

In addition to membrane technology, cold vaporization, ion exchange encapsulation and chemical treatment systems can be used to purify cleaners and rinses so that they can be reused.

Disposal - When it comes to disposing a cleaner bath, there are a few options:

- discharge to a holding tank from which the waste is subsequently pumped and hauled by a licensed hauler for appropriate disposal at an approved facility;
- discharge to surface waters or groundwater if permitted or exempted by the Michigan Department of Natural Resources (MDNR) under the Michigan Water Resources Commission Act (Act 245 of 1929); or
- discharge to a Publicly-Owned Treatment Works (POTW) with the approval of the POTW.

Approval for discharging to a POTW, surface water or groundwater may be contingent upon pretreating the waste to remove the oils and grease and adjusting the pH and removing organic matter and dissolved metals. Refer to the "Environmental Regulatory Considerations" section of this fact sheet for more details.

Even though the cost of equipment to recover and treat aqueous cleaners can be expensive, the same equipment could be used on other waste streams generated at your business such as machining coolants and mop water.

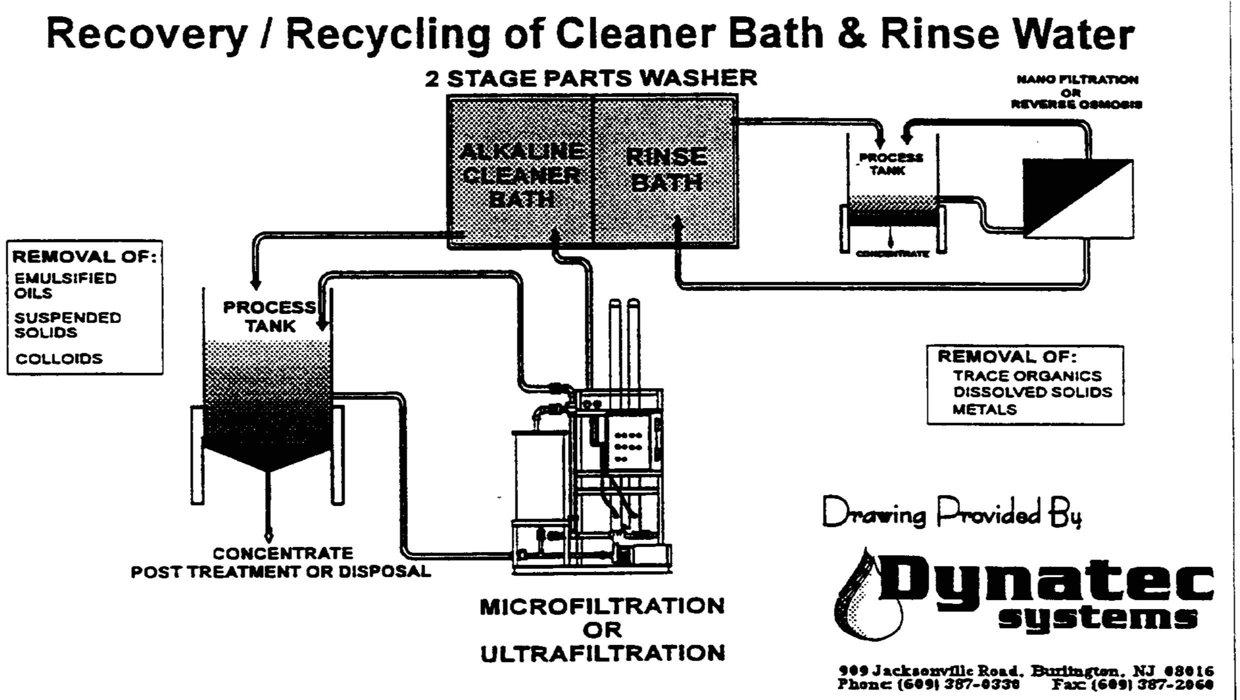
Semi-Aqueous Cleaners

- *How do They Work?*

Semi-aqueous cleaners, also known as emulsion cleaners, are nonchlorinated hydrocarbons dispersed in water with or without the aid of emulsifiers. They, therefore, have the cleaning properties of solvency and detergency.

Whereas the cleaning phase for aqueous cleaners occurs in one step, the cleaning phase for semi-aqueous cleaners generally occurs in two steps. The soil and contaminants are dissolved in the primary tank containing the cleaner. In the secondary tank, the soil/cleaner

FIGURE 1.



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Dynatec systems
909 Jacksonville Road, Burlington, NJ 08016
Phone (609) 387-0330 Fax (609) 387-2060

mixture is rinsed off the part with water. Like aqueous cleaning, the parts then proceed through the rinsing and drying phases.

Due to their solvency properties, semi-aqueous cleaners are effective in removing heavy greases and waxes. They traditionally have been used as an in-process cleaner, removing the bulk of the soils so that further manufacturing can be conducted without difficulty.

•*Composition*

There are two basic components of semi-aqueous cleaners, and they are categorized by their ability to mix with water. Water immiscible components include:

Terpenes - These are natural hydrocarbons derived from plants. d-Limonene is extracted from the rinds of lemons and oranges. Pinene is extracted from the bark of pine trees.

Esters - Aliphatic monobasic esters and dibasic esters are used in semi-aqueous cleaners.

Water miscible components of semi-aqueous cleaners include:

Glycol ethers - There are two common kinds of glycol ethers: e and p series. The p-series are typically used in cleaning formulations because they are safe for personal contact and not regulated under Section 313 of the Emergency Planning and Community Right-to-Know Act.

Ketones - Commonly used ketones in cleaning are acetone and methyl ethyl ketone.

Alcohols - Commonly used alcohols used in cleaning are ethanol and isopropyl alcohol.

Amines - N-methyl-2-pyrrolidone (NMP) is an amine that is used in paint strippers as a replacement for methylene chloride.

Surfactants - See Page 4 for definition.

Alkaline Builders - See Page 6 for definition.

•*Methods of Application*

Immersion is the most common method of contacting the part with the semi-aqueous cleaner. Because of the relatively low flash point of organic solvents, terpenes in particular, there are limitations to the degree of heating and agitation applied to the cleaning tank.

To avoid ignition of solvent vapors, it is recommended that a minimum of 30° F is maintained between the operating temperature of the cleaner and its flash point. Terpenes, which have a flash point in the range of 115° to 120° F, should not be heated above 90° F unless diluted with water. Glycol ethers and NMP have flash points of 142° and 204° F, respectively.

Although agitation increases cleaning efficiency and emulsion stability, care must be taken to avoid creating mists of concentrated semi-aqueous cleaners. These mists can be ignited at room temperature.

•*Safety*

In addition to the flammability concerns identified above, there are some worker safety concerns associated with terpene cleaners. Since they are derived from plants, they can have an odor that is bothersome to some workers. Ventilation systems may have to be provided in areas where the cleaners are used.

Toxicity studies on terpenes as well as other cleaner components are being conducted. According to an EPA report entitled Aqueous and Terpene Cleaning Interim Report, "... aqueous and terpene cleaners can be used in a manner safe to workers, consumers, and the general population given appropriate technological changes and exposure control practices."

Since the cleaners are moderate skin irritants, solvent resistant gloves and aprons and eye protection should be worn where exposure is likely. Handling and safety requirements identified in the cleaner's Material Safety Data

Sheet (MSDS) should be followed without exception.

•*Cost*

Terpenes, esters and glycol ethers are priced at $10 to $18 per gallon when purchased in drum quantities. NMP's cost is $25 to $30 per gallon.

•*Recovery and Disposal*

Recovery - Since oils tend to dissolve in semi-aqueous cleaners, skimmers and coalescers are not as effective in the removal of these contaminants. Concentrated semi-aqueous cleaner baths are not reclaimable. Contaminants dissolve and become locked up in the hydrocarbon solvent making separation of the dirt from the cleaner difficult. Once they become contaminated, the cleaning bath must be disposed. The rinse waters of the semi-aqueous cleaning system can be recycled by microfiltration membranes or ion exchange.

Disposal - The disposal options for semi-aqueous cleaning baths diluted with water are the same as those identified for aqueous cleaning baths. Concentrated semi-aqueous cleaners, because of their high BTU value, may be picked up by a licensed hauler and taken to approved facilities that process wastes into a fuel that is burned for energy recovery.

Rinsing Step

To obtain the required level of cleanliness, parts exiting the aqueous or semi-aqueous cleaning bath should be rinsed. Rinsing is necessary to remove the residual layer of contaminants and cleaner. Not all cleaners rinse the same. Semi-aqueous cleaner residue is more difficult to remove than aqueous cleaners. The level of rinsing ranges from simple immersion or spray using tap water to multiple rinse tanks using deionized water.

To minimize water usage, a counterflow rinsing system should be used. In a two tank counterflow system, water in the final or secondary rinse tank is used to replenish the initial or primary rinse tank.

Heat, agitation and chemical additions will increase the effectiveness of rinsing. Rinse water should be warm as opposed to hot or cold. Hot water may set some of the residues on the part or form oxide films. Temperature also affects the surface tension of water. More droplets will cling to parts rinsed with cold water than with warm water. Ultrasonics or pumps provide the mechanical action necessary to increase rinsing efficiency. Consideration should be given to using deionized water for rinsing parts, which eliminates the spotting caused by the salts found in hard water. Adding isopropyl alcohol to the rinse water improves rinsing by reducing the surface tension of the water.

Drying Step

Unlike solvent vapor degreasing, in which parts come out dry, aqueous and semi-aqueous cleaned parts are wet. Drying can be accomplished by a variety of methods depending upon part configuration and the speed required. Typical methods of drying include evaporation, mechanical displacement of water or displacement using another fluid.

Evaporation under ambient conditions is slow and can lead to rusting. Evaporation is accelerated by putting the parts in a chamber that circulates heated air. Air knives blow off water from the part with compressed air. It minimizes the deposition of dissolved solids that may remain on the part. Centrifugal drying spins water off. Special protective oils displace water from the part and replace it with a film that prevents corrosion.

ENVIRONMENTAL REGULATORY CONSIDERATIONS

Waste streams generated from aqueous and semi-aqueous parts cleaning systems can include used oils, wastewater (cleaning baths and rinse waters) and even some small amounts of volatile organic compounds (VOCs). In general, the options for wastewater disposal are: (1) contracting with a hauler to deliver it to a commercial treatment and disposal facility, or (2) pretreating the wastewater on-site prior to discharge to a POTW or other approved receiver. On-site pretreatment may generate sludge, which is another waste stream requiring disposal. The environmental regulatory considerations for all of these waste streams are discussed below.

Used Oils

Used oils that are separated from cleaner solutions by devices such as skimmers and coalescers can be disposed in the same manner as other used oils that may be generated from other production or maintenance processes. If the used oil is recycled, the generator is exempt from the requirements of Michigan's Hazardous Waste Management Act, 1979 PA 64, as amended (Act 64).

If the used oil will be burned for energy recovery, the generator will be subject to the hazardous waste requirements under Act 64. Used oil destined for burning is identified as either on-specification or off-specification. Used oil is considered to be "off-spec" unless laboratory results or other documentation shows that contaminant levels do not exceed specifications. For more information regarding the requirements for this management option, contact your nearest Michigan Department of Natural Resources' (MDNR) district office.

All generators of used oil must comply with the management standards promulgated under special authority of the federal Resource Conservation and Recovery Act (RCRA), Section 3014(a). These standards were issued to control potential risks from recycled used oil and, according to these requirements, a generator must:

- Keep storage tanks and containers in good condition;
- Label storage tanks, "used oil";
- Clean up any used-oil spills or leaks to the environment; and
- Use a transporter with an EPA identification (ID) number when shipping used oil off-site. The transportation of used oil in Michigan is also subject to the requirements of Michigan's Liquid Industrial Act, 1969 PA 136 as amended (Act 136). A contract hauler of liquid industrial waste, regardless of whether or not the material is hazardous, must be licensed and a manifest must accompany the shipment.

Wastewater (Off-site Treatment & Disposal)

Before sending spent cleaners (or liquid industrial waste) to an off-site facility for treatment and disposal, it is the generator's responsibility to determine if the waste is a hazardous waste. There are two categories of hazardous wastes: listed and characteristic. Listed wastes are waste materials listed by name in either Act 64 or the Resource Conservation and Recovery Act (RCRA). Characteristic wastes are wastes that possess any of the characteristics identified in state and federal hazardous waste law. These characteristics include corrosivity, ignitability, reactivity, toxicity and severe toxicity.

If the wastewater is determined to be non-hazardous, it is not regulated under Act 64 or RCRA. However, like used oil, the transportation of the wastewater is subject to Act 136.

If the liquid industrial waste is determined to be a hazardous waste, it is subject to all applicable requirements pursuant to state and federal hazardous waste regulations. This would include transporter licensing and disposal at a licensed hazardous waste treatment, storage or disposal facility (TSDF).

Depending on the hazardous waste characterization and amount of recoverable oils, liquid industrial wastes will typically go to one of three types of facilities.

Used oil processors will treat non-hazardous liquid industrial waste containing recoverable oils in addition to processing used oils. The used oils are separated from the wastewater and are processed for fuel use or non-fuel industrial uses, such as cutting and honing oils. The treated wastewater is discharged to a POTW.

Licensed hazardous waste TSDF facilities will process both non-hazardous and hazardous liquid industrial wastes containing recoverable oils. The used oils are reclaimed and the treated wastewater is discharged to a POTW. A price break is given to non-hazardous liquid industrial wastes.

Licensed hazardous waste TSDF facilities will solidify both non-hazardous and hazardous liquid industrial wastes. The solidified material is landfilled. This disposal option is best suited for wastes that are heavily contaminated and/or have very little BTU value.

Wastewater (On-site Pretreatment)

Businesses must sometimes pre-treat chemical wastes prior to disposal. The level of pretreatment depends upon the quantity and nature of the contaminants and the limitations imposed by the POTW if discharged to a sanitary sewer; the National Pollutant Discharge Elimination System (NPDES) permit if discharged to surface waters; or state groundwater permit if discharged to the groundwater.

There are two types of national pretreatment standards that control pollutants introduced into a POTW: prohibited discharge standards and categorical pretreatment standards. Prohibitive discharge standards are contained in the general pretreatment regulations, which are found in Title 40, Part 403 of the Code of Federal Regulations (40 CFR Part 403). These standards are designed to prevent pass through or interference with the treatment processes at the POTW. Categorical pretreatment standards regulate the level of pollutants discharged to the POTW for specific types of industries. The categorical pretreatment standards appear in 40 CFR Parts 405 through 471.

pH Adjustment - Since aqueous cleaners are alkaline and have a pH ranging between 7 to 12, pH adjustment may be required prior to sanitary discharge. Sulfuric or hydrochloric acid are typically used to lower the pH.

Biodegradable - Many manufacturers claim their aqueous and semi-aqueous cleaners are biodegradable. This can be somewhat misleading because the term biodegradable applies only to the cleaner. It does not apply to the contaminants in the cleaner. Also, some surfactants take too long to break down into the constituent elements to be environmentally acceptable. If the amount of dissolved metals and/or emulsified oils in the waste stream exceeds the POTW, NPDES or groundwater permit discharge limits, they will have to be removed from the waste stream prior to discharge.

Free Oil Removal - Free oils will rise quickly to the surface of a nonagitated tank. Skimmers have either a rope or drum that lifts the oil from the surface of the cleaner and deposits it into a holding tank. Devices such as coalescers and centrifuges will improve the separation of free oil from the cleaner.

Emulsified Oil and Metal Removal - Removing dissolved metals and emulsified oils from aqueous cleaners can be achieved through chemical treatment or membrane separation. The chemical removal of stable oil-water emulsions and dissolved metals occurs in three steps:

(1) a coagulant is added to break the oil-water emulsion and a hydroxide, such as lime, precipitates out the dissolved metals;

(2) a flocculent is added to agglomerate the tiny oil particles and metal precipitate into particles; and

(3) the particles are separated from the clean water through sedimentation and removed. The chemical treatment of wastewater generates sludge, which is typically dewatered prior to disposal.

Reverse osmosis can remove dissolved metal ions from the cleaner solution. Ultrafiltration membranes can remove emulsified oils.

Sludge Removal - Pretreatment of wastewater may result in creation of a sludge. The sludge must be evaluated to determine if it is sufficiently dewatered and if it is a hazardous waste. If the sludge has been determined to be non-hazardous waste, it can be disposed in a sanitary landfill licensed under Michigan's Solid Waste Management Act, 1978 P.A. 641, as amended (Act 641). Liquid waste cannot be landfilled.

Air Contaminants

Michigan's Air Pollution Act, 1965 P.A. 348, as amended (Act 348) regulates sources of air pollution. According to Rule 201, "... a person shall not install...equipment...which may emit an air contaminant unless a permit to install ...is issued."

Aqueous and Diluted Semi-Aqueous Cleaners - Parts washing processes utilizing aqueous cleaners and semi-aqueous cleaners diluted with water could meet one or all of the following permit exemptions.

Rule 281 (d), "the permit system does not apply ... to equipment used for washing or drying materials, where the material itself cannot become an air contaminant, if no volatile organic compounds are used in the process and no fuel is burned."

Rule 285(i)(iii), "the permit system does not apply to ... equipment for surface preparation of metals by use of aqueous solutions, except for acid solutions."

Rule 285(o)(iv), "the permit system does not apply to ...equipment used for ... cleaning ... if the process emissions are only released into the general in-plant environment."

Undiluted Semi-Aqueous Cleaners - Semi-aqueous cleaners used in concentrated form could meet the permit exemption identified in Rule 285(o)(iv).

Although aqueous and certain semi-aqueous cleaning systems are exempt from permitting requirements, all cleaners are still subject to Parts 6 and 7 of the Act 348 rules, which regulate the usage of VOCs in existing and new cold cleaners, respectively. The rule requires that the equipment meet various design criteria and good operating practices to minimize the release of VOCs.

For more information concerning:

- The disposal of solid and hazardous wastes and the transportation of liquid industrial wastes, contact the Waste Management Division in your local MDNR district office.
- The NPDES requirements, contact the Surface Waster Quality Division in your local MDNR district office.
- Discharges to sanitary sewers, contact your POTW.
- The regulation of air contaminants, contact the Air Quality Division in your local MDNR district office.
- Suppliers of semi-aqueous cleaners and aqueous parts washing equipment, contact the Environmental Services Division, Departments of Commerce and Natural Resources.

Michigan Department of Natural Resources Environmental Protection District Offices

Marquette	(906) 228-6561
Cadillac	(616) 775-9728
Gaylord	(517) 732-3541
Grayling	(517) 348-6371
Bay City	(517) 684-9141
Grand Rapids	(616) 456-5071
Shiawassee	(517) 625-4600
Plainwell	(616) 685-9886
Jackson	(517) 780-7900
Livonia	(313) 953-0241

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For more information on waste reduction for businesses and the Small Business Clean Air Assistance Program, contact the:

Environmental Services Division
Michigan Departments of Commerce and
Natural Resources
P.O. Box 30004
Lansing, Michigan 48909
(517) 335-1178

Toll Free:
1-800-NO-2-WASTE

October 1994
#9409

Semi-Aqueous Cleaning: Is It for You?

How clean do your parts need to be? The answer will help you decide...

By John Durkee, II
President
Creative EnterpriZes
Lake Jackson, Texas

Something old, something new, something borrowed, something big and blue. That expression describes semi-aqueous cleaning, sort of. Displacement drying with immiscible fluids has been used for many years. The new aspects are the surfactant packages, which allow excellent solvency in the cleaning stages and efficient separation of cleaners from rinses in the decanter stages. Purifying recycled water with membrane technology was borrowed from the waste treatment and water purification industries. And finally, the main application for semi-aqueous cleaning seems to be cleaning of computer components, hence "Big Blue."

Unfortunately, semi-aqueous technology probably has been oversold. Common opinion is that it is overpriced. This is because both cleaning agent and equipment suppliers naturally have attempted to expand their technology from the electronics to the metals industry. Since the needs and values of both markets are different, that expansion was not very successful.

How semi-aqueous cleaning agents work. There are two types of semi-aqueous cleaning agents. They differ based on how they are separated from the water rinses.

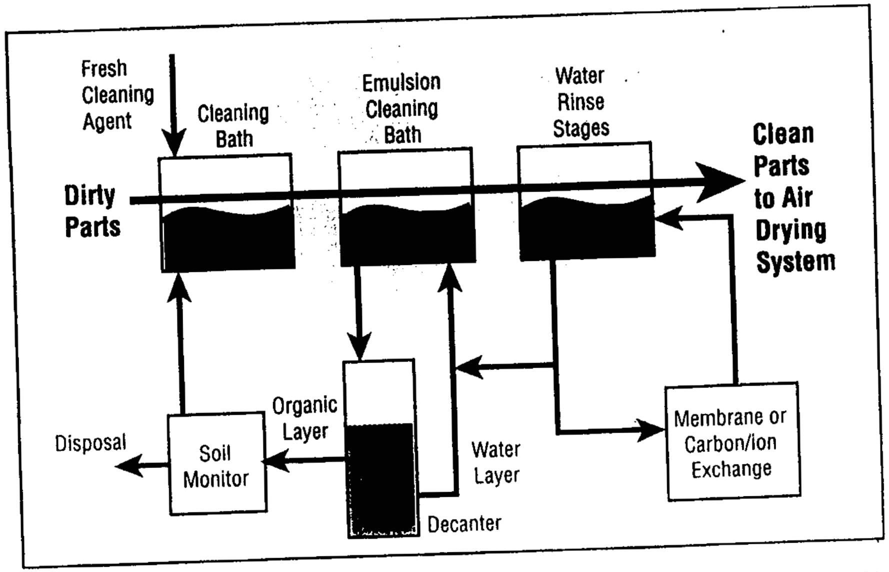
Two approaches are used. 1) Separation by gravity, based on immiscibility of solvents and rinse water. 2) Separation by boiling point difference, based on distillation of water-soluble solvents and rinse water.

Within these two types there are various products formulated from different solvent bases. In general, the suppliers of semi-aqueous cleaning agents are producers of the solvents included in their products.

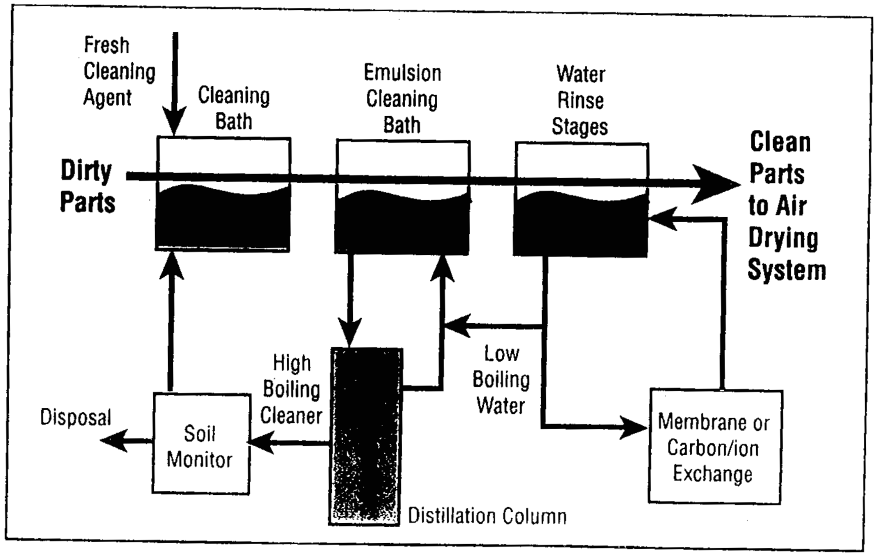
Semi-aqueous processes. The fundamental semi-aqueous process is as follows: 1) Parts are cleaned with a suitable solvent. The solvent is removed from the parts by washing with progressively cleaner water. 2) Parts are dried with forced hot air. 3) Cleaning agent and detergent are separated from the rinse water either by gravity or distillation. Rinse water may be purified with membranes for recycling. 4) Processes are shown in Figure 1, separation by gravity, and Figure 2, separation by distillation.

Is semi-aqueous right for you?

1. SEPARATION by gravity



2. SEPARATION by distillation



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Usually the semi-aqueous process is used to precision clean small parts. The cost of removing incremental soils is high. Large parts seldom have to be precision cleaned.

Although the semi-aqueous process could be used for rough in-process cleaning, its investment, cost, and space requirements make that prohibitive.

The semi-aqueous cleaning process is the right choice for you if your parts must be totally clean. Relevant applications include high-value situations like circuit boards, disk drive heads, components for military guidance systems or components for precision instruments.

Alternately, precision cleaning can be accomplished with several other cleaning agents and processes. Some costing less.

The semi-aqueous cleaning process will be the right choice for you when the cost of meeting environmental regulations justifies the cost of internal waste recovery.

The basic rule for solving cleaning problems is to match the cleaning process options to the parts and match the cleaning agent to the soil.

Process considerations. A major advantage of semi-aqueous cleaning is the high degree of waste recovery. The only direct waste is a concentrate of the soil in the cleaning agent. A major disadvantage is complexity, relative to vapor degreasing, so equipment will be expensive.

Semi-aqueous technology may be practiced either in batch or continuous mode. Often in batch mode the cleaning tank and successive tanks are located on top of a bench. An operator moves baskets of parts from one tank to the next one according to a preset time schedule or inspection. Or in continuous mode, parts are relocated from one tank to the next using an automatic or semi-automatic system.

Cleaning tank. The cleaning tank is outfitted as would be necessary with any other cleaning system. Operating temperatures range from ambient to 120F. Soil concentration at equilibrium should be no more than five to 10 pct of the weight. Contact time is probably 30 seconds to five minutes. Ultrasonics are often used to remove particulates.

As parts are removed from the tank, they pass an air knife that blows off cleaning agent. This is done to adjust the soil concentration in the cleaning stage and adjust the cleaning agent concentration in the next emulsion cleaning stage. Too little blow off will harm cleaning performance by raising the soil concentration in the cleaning stage and reducing the cleaning agent concentration in the next emulsion cleaning stage.

Emulsion rinse tank. Water is sprayed onto the parts in the emulsion cleaning stage. This is done to remove cleaning agents and continue the cleaning process with a water emulsion of the cleaning agent. The water emulsion is often a better cleaner than the material in the cleaning stage because little soil is present

TABLE I—Representative Semi-Aqueous Cleaning Agents

Solvent Materials	Commercial Product	Type of Separation
Aliphatic Hydrocarbons	Axarel™ (Du Pont) Actrel™ (Exxon)	Gravity
Ester Additive (can be used pure)	Axarel™ (Du Pont) Actrel™ (Exxon)	Gravity
Terpene (D-limonene)	Petrofirm, Envirosolv, Florida Chemical, Glidco	Gravity
Tetrahydrofurfural Alcohol	Kyzen	Distillation
Hydroxy (glycol or alcohol)	Dow	Distillation
Specialty	PartsPrep™ (IPS) NMP (BASF)	Distillation

in the emulsion cleaning stage. The temperature is slightly increased and contact time is in the same range.

Cleaning agent concentration in water is from one to 10 pct. This is deliberately low to minimize organic cleaning agent flow into the final rinsing stages.

The emulsion material is fed to a decanter or distillation column for separation.

Conditions in the decanter are deliberately different from those in the cleaning and rinse tanks. Usually the temperature is 20 to 40F higher. Separation requires five to 30 min.

An interface monitor in the decanter is used to activate pumps that withdraw the top organic phase and the bottom water phase. Removal is usually done in batch mode to maintain the organic/water interface between prescribed levels.

Problems occur in a decanter system when the withdrawal of one phase becomes contaminated with the other phase. A change in soil chemistry can be a major cause of contamination. Another is foaming in the rinse tank, which can occur if spray nozzles are not correctly sized and positioned.

Distillation separates chemicals based on differences in their boiling points. For the chemicals listed in Table I and water, the difference is more than 70C. That is well above a minimum of 10 - 15C acceptable for good operation. Further, the boiling point of soils are 200C above the boiling point of water.

The key advantages of a distillation separation system are reproducible and forgiving separation of soil from the rinse water and water from the cleaning solvent.

Operation could be either batch or continuous, depending on the cleaning load. Batch distillation systems probably are less expensive.

Distillation requires more capital and consumes more energy than decanting. However, distillation is a more positive separation approach than decanting. It can be more easily monitored and is less affected by changes in soil chemistry. Since the separation stage is the keystone of a semi-aqueous process, the opportunity to avoid problems in that stage is worthwhile.

Final rinse tanks. In these tanks contamination includes original unremoved soil and possibly residual components of the cleaning agent.

The final rinse stages usually involve only water. Although plain water probably will not remove soil or solvent, the final rinse stages are the last opportunity to affect cleaning process quality.

Water is sprayed through nozzles to contact all external and internal surfaces. The water removes soluble components of the detergent package. Contact time is usually shorter than the contact in the previous stages. Occasionally ultrasonics are used to enhance contact of the water with part internals.

Rinse water cascades from the final rinse stage to the initial rinse stage. Usually there will be one to two stages needed to achieve the required cleansing of components, and then a final stage with fresh rinse water. To avoid water spotting, the last one or two stages should use DI water.

Drying Process. The drying process is based on the character of the parts and the degree to which they need to be dried. No consideration is given to the type of separation.

Usually forced hot air is used to dry water from parts. If parts have complicated internals, a centrifugal dryer or a displacement dryer will be needed.

Water recovery. Materials in the rinse water are water-soluble soil components such as fluxes or salts, soluble detergent components and insoluble particulates. A cartridge filter is used to remove the latter from rinse water.

The primary membrane type used in cleaning systems requires a difference of at least a factor of 10 between the molecular size of the materials to be rejected and the molecular size of water, which passes through the membrane. Since the water molecule is very small, this means the molecular weight of materials that can be rejected is around 200. Better than 99 pct rejection of impurities can be achieved with multiple membrane stages.

The clean water (permeate) is recycled to the rinse stages. The reject stream is held and gradually consumed by blending with the initial rinse materials. Occasionally a purge is required.

Product considerations. The cleaning agent is a mixture of at least two generalized components, solvent(s) chosen to match solubility characteristics of the soil plus surfactant.

There are a variety of ways in which the solvent(s) can be matched to the soils. One is experience. Another is scouting tests with a variety of solvents and typical soils. The most inexpensive approach is to conduct solubility tests to determine the solubility parameters of typical soils.

Gravity Separation. It is in the decanter stage that the chemical manufacturer's skill is revealed. The detergent package must complete these functions: 1) Permit rapid and complete emulsification of the cleaning solvent with soil in the cleaning tank, or soil will be left on the parts. 2) Permit emulsification of the cleaning solvent and soil with water in the emulsion rinse tank, or cleaning solvent will be left on the parts. 3) Permit de-emulsification of the cleaning solvent and soil from water in the decanter, or both soil and cleaning agent will be left on the parts. 4) Inhibit solution in the water of the detergent package under the conditions of the decanter, or the water recycling system won't perform efficiently.

This performance is dependent on type and amount of soil, and has sometimes been fragile and difficult to replicate. Some users have found that if their soil changed, the total performance of their semi-aqueous cleaning system changed. Unfortunately, a soil change is not always a deliberate one. Others have found cleaning or rinsing performance to depend strongly on the consistency of fluid mixing.

Distillation separation products. Detergent or surfactant packages also are added to these solvents. However, their function is to improve wetting of the solvent on the parts or improve rinsing of the solvent from the parts. In many cases, the selection of the detergent is related to the nature of the soil.

There are various solvent materials available among gravity-separation and distillation-separation types of semi-aqueous cleaning agents.

Product costs. Semi-aqueous cleaning agents are expensive, ranging from two to four dollars per pound. So filling a cleaning system can be expensive.

On the other hand, replacement costs are often low. If the cleaning system is working properly, cleaning agent is lost only through evaporation and with the soil. There are many case histories where a user converts to a semi-aqueous cleaning system and buys no replacement cleaning agent for a year or more!

The preceding descriptions should have prepared you for "sticker shock." A small four-stage semi-aqueous batch cleaning system will cost $50,000 to $75,000. The higher price includes ultrasonics. Some suppliers provide a "dishwasher" that automates the batch cleaning steps. Cost is around $100,000.

Machines for larger parts will cost more, as will machines for continuous cleaning. A price of $250,000 would not be surprising. Water recovery systems will require $10,000 to $25,000 additional.

Can semi-aqueous technology be implemented more cheaply? Yes. One reason for the high costs is recovery of high development expenses. After 1995, when conversion from CFCs is complete, prices will surely decline as does demand. You can save some money by not automating the cleaning steps. You can save more if you can dispose of rinse water locally without significant cost.

Don't forget that price and needs are bound together. In less than five years, these expensive semi-aqueous cleaning machines have become the world standard for cleaning electronic components and circuit boards without CFCs. If you need precision cleaning, and value environmental security, semi-aqueous technology is worth the high cost.

Alternatives to semi-aqueous cleaning. Other ways to achieve precision cleaning include:

- Cascade multiple-stage cleaning with a high boiling solvent followed by displacement drying.
- Chlorinated cleaning agents such as perchlorethylene in an enhanced vapor degreaser.
- Perfluorinated compounds and HFCs supplemented with special surfactant.
- Contained cleaning with volatile low-boiling solvents such as isopropyl alcohol.
- Co-solvent machine cleaning where an appropriate solvent is used in multiple-stage cleaning and an immiscible material is used as a drying agent.

All of these approaches must be customized. A choice depends on the details of your situation.

You are the one who best knows if part contamination imposes significant cost to your production or maintenance. If you do, semi-aqueous cleaning is a prime option, as may be other approaches listed above.

The way to get started is to first focus on your soil, and then focus on your parts. Start discussions with two chemical suppliers and/or a consultant. Select one supplier of each of the gravity-separation and distillation-type. Work with those suppliers to conduct cleaning trials with your soils and parts. From the results, choose one of the two methods.

Then open discussions with two suppliers whose equipment best fits your parts and automation needs. Work with each to develop a process and a financial proposal.

Choose the proposal based on degree and quality of support rather than price.

Semi-aqueous cleaning has been established as the "world standard" approach in the global electronics industry. If you need precision cleaning, this is the most common choice. Systems are highly customized, and can offer recovery of nearly all process fluids except the soil. Be prepared to spend capital on equipment and initial inventory, but expect excellent cleaning. PF

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OhioEPA

State of Ohio
Environmental Protection Agency

Fact Sheet

Pollution Prevention

Extending the Life of Aqueous Cleaning Solutions

Number 31
September 1995

The bath life of an aqueous cleaning solution is limited by the buildup of the contaminants removed from parts. Although the cleaners may avoid some of the environmental issues associated with cleaning with organic solvents, the periodic disposal of the bath to maintain part quality results in its own environmental and economic problems. These problems can be minimized through techniques to extend the life of and recycle aqueous cleaning baths.

Don't Trade One Problem for Another

In recent years, a number of companies have switched from cleaning using chlorinated solvents, such as 1,1,1-trichloroethane or trichloroethylene, to cleaning using aqueous solutions. These cleaners are water-based solutions that can contain a number of chemical components such as detergents, surfactants, saponifiers and rustproofing inhibitors. They are typically used in multi-stage systems, which may involve immersion, sprays, ultrasonics, rinsing, drying or other steps.

Two of the key motivators for finding alternatives to solvent-based cleaning are avoiding or minimizing the air emissions and hazardous waste generation associated with these processes. However, a company that switches to an aqueous cleaner may find itself with a new problem in a new environmental media. Both the components of the cleaner and the contaminant (typically oils and greases) are now introduced into the wastewater.

Fortunately, the impact of aqueous cleaning on wastewater can be minimized. Extending aqueous cleaning bath life through operating changes and/or through recycling may offer an environmentally sound alternative. It may also reduce costs, allowing cleaning solutions to be reused repeatedly, instead of becoming simply a wasted valuable raw material.

Companies that are currently in the process of selecting a new aqueous cleaning system may want to consider recycling options early in the selection process. This will help them select proper cleaning equipment and a cleaning solution that both effectively cleans parts and can be recycled in the most cost effective manner.

The Problem of Contaminants

The life of a cleaning bath will be limited by the build up of contaminants as they are removed from the parts. With time and use, cleaning effectiveness will be reduced (Lindsey et all, 1994).

There are many options for maintaining cleaning baths and extending their lives. The option that will be most effective and feasible will be determined by a number of factors, including the volume and number of the baths, and the contaminant or contaminants most responsible for degrading the quality of the bath. This can include non-emulsified oil, emulsified oil, ions such as sodium or chloride, suspended solids and dissolved solids.

One of the most significant factors is whether the oil is emulsified, and how it became emulsified. Oil can become emulsified by a variety of factors such as heat, agitation or the chemical components of the aqueous bath. Some options only address non-emulsified oil, some can also remove oil that is mechanically emulsified, and some can even remove chemically emulsified oil.

Mechanically emulsified oils are oils that have been broken apart by physical forces, such as agitation or heat, during cleaning operations. Over a period of time, if these physical forces are removed, these oils may separate out by themselves. This process can be accelerated by equipment such as coalescers or separators, discussed later in this fact sheet.

More sophisticated recycling equipment can remove even chemically emulsified oil. This is oil which has been suspended by components of the cleaner, which were specifically designed to emulsify and suspend this oil to avoid redeposition (Peterson, 1995). Equipment to remove these oils is typically the most capital intensive of the systems discussed in this fact sheet.

Office of Pollution Prevention, Ohio Environmental Protection Agency, P.O. Box 1049, Columbus, OH 43216-1049, (614) 644-3469

Extending the Life of Aqueous Cleaning Solutions

Because of the problems inherent to removing chemically emulsified oil, the chemical make-up of the cleaning bath used will partially determine which systems are necessary to adequately remove the oil.

A cleaning solution which has less power to chemically emulsify the oil will inherently have less cleaning ability. Increasing the ability of the cleaner to remove oil results in a trade-off of decreasing ability of the oils to be easily separated from the cleaner at a later point in time for recycling purposes (Durkee, 1994).

Extending Bath Life Prior to Recycling

Some options do exist for extending the life of an aqueous cleaning bath without the purchase of additional equipment such as recycling systems. These options are discussed below.

Reduce sources of contamination - Some contaminants, such as metal-working fluids or fingerprints, can be reduced at the source through operating changes or increased care in handling during the processes prior to the cleaning stage. Some material, such as a rust protectant which a supplier intentionally puts on a metal part, becomes a contaminant at a later point and has to be removed. The company performing the cleaning should carefully consider its inventory practices to determine if any of this contamination can be avoided or minimized.

Reduce heat and turbulence during off-hours - Reducing the heat and turbulence in aqueous baths during the night or off-hours may result in more of the mechanically emulsified oil rising to the top of the bath. This will allow more of the oil to be skimmed in the morning before operations begin.

Partial bath replenishment - A company may be able to extend bath life by only partially dumping baths and adding fresh water and chemicals to bring the solution up to volume. This may increase the effectiveness of the cleaning bath sufficiently for continued cleaning. Eventually, however, chemicals will need to be added at a rate that results in costs greater than the savings from dumping the bath and mixing a new solution. This indicates that the entire bath should be dumped and refilled (PRC Environmental, 1989).

Recycling

Many different types of systems exist to separate oil and other contamination from the aqueous cleaning baths. During discussions with equipment vendors it is important to emphasize the following: the company's intention to reuse the aqueous baths, not simply pretreat them before discharging; the temperature of the baths; and the pH of the baths.

The company will also need to determine the combined volume of the cleaning tanks and the average time between tank changeout, and should prepare copies of material safety data sheets. It should also consider analytical testing to determine whether the primary contamination is chemically or mechanically emulsified oil, non-emulsified oil, suspended solids, dissolved solids, or other type of contaminant. Some vendors will conduct this testing themselves.

Filtration

Literature indicates that in-tank filter cartridges can extend bath life. Filters can be selected to remove **non-emulsified oils or solids, but not emulsified oils.**

One company reported the purchase of used filtration equipment for $500 with installation costs of $350 for filtering an electrocleaner and acid pickle (105 gallons each). They estimated that the filtration extended the life of the electrocleaner by 10 times.

The results of a user survey in the book, "Pollution Prevention and Control Technologies for Plating Operations" indicated that of 265 alkaline soak processes, 21 utilized in-tank filtration and one used external filtration for bath maintenance (Cushnie, 1994).

However, some experts indicate that the cleaning ability of filters is insufficient to make a significant change in bath life because of their inability to remove any emulsified oil. One vendor indicated that filters may become coated so quickly with oil that the cost of either replacing or washing the filters might outweigh the financial benefits of extended bath life.

Experimentation with filters may indicate whether or not they significantly increase bath life for a particular application.

Mechanical separation of oil

Several different types of equipment exist to separate certain oils from the cleaning solutions.

Decantation - High volumes of **non-soluble oil (only)** can be removed through decantation of the oily cleaning solution while in a holding tank. These systems should be designed to prevent oil from being circulated through process pumps, so the pumps can not further emulsify the oil. Collected oil can be skimmed into a decanting chamber where a more complete separation can be achieved. (Temple, 1990).

Separation - Both non-emulsified oil and mechanically-emulsified oil (but not chemically emulsified oil) can be removed through a separation unit (this may be referred to as a plate separator, a gravity separator or a coalescing unit) or a combination of filtration and a separation unit. Separation units can be central or dedicated, and can take up relatively small amounts of space.

These units speed up the natural separation of mechanically emulsified oil by agglomerating oil droplets. This causes them to separate from the cleaner due to differences in density (Peterson, 1995).

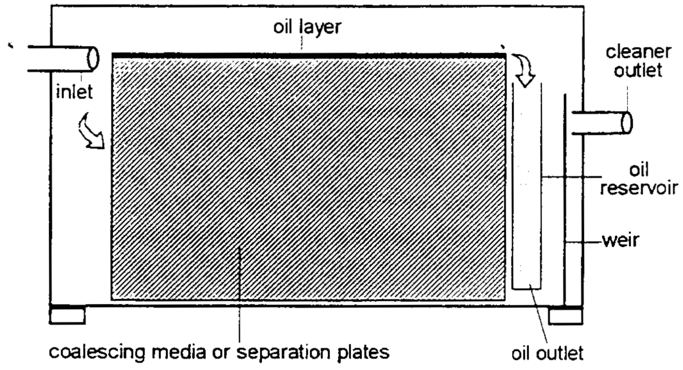

Figure 1: Separator

Although the variety of separation units available function in essentially the same manner, they will differ greatly from each other based on the vendor and on the specific needs of the customer. See Figure 1 for an example of a generic separation unit.

One advantage of combination filtration/separation systems is that they do not risk removing the additives in the aqueous bath, as membranes filtration systems sometimes do.

One electrical component manufacturer switched from simple manual skimming to a separation system. The vendor analyzed a sample of the used bath to determine the internal configuration of the coalescing unit. The system was installed for less than $10,000 and resulted in a first year savings of more than $29,000 chemical costs (Batutis, 1989).

Membrane Technologies

In traditional filtration, the entire stream is passed through a filter. Crossflow filtration, typically used for ultrafiltration and microfiltration, flows the stream across a membrane using pressure to force filtration to occur. See Figure 2 for a diagram of crossflow filtration. Ultrafiltration and microfiltration may offer effective means to remove contaminants and increase bath life. They may also be the most capital intensive options discussed in this fact sheet. The type of membrane system chosen depends on factors such as the most significant type of contamination, the volume of fluid to be processed, and the temperature of the solution.

Suspended solids may need to be removed prior to ultrafiltration, which is capable of removing **dissolved solids and/or mechanically or chemically emulsified oil.** It removes particles in the 0.005 - 0.1 micron range.

Many membranes are not compatible with hot and/or caustic solutions. This may preclude use of these systems entirely, or necessitate the use of a holding or cooling tanks, which would require extra floor space. Ultrafiltration may require some type of pretreatment, either by filtration or by oil separation. For instance, a vendor may provide packages with attached filtration for suspended solids. Or, the system may use a tramp oil separator for pretreatment to remove mechanically dispersed and free oils. Which system is best can only be determined after testing and through communication with vendors.

Microfiltration removes particles in range of 0.1 to 5 microns. Many microfiltration systems are available with ceramic filters that can withstand the high temperatures and caustic solutions associated with many cleaning baths. This may avoid the need for a holding tank or cooling tank, saving floor space. A microfiltration unit may take up less space than an office desk.

Microfiltration can remove **solids, non-emulsified oil, or mechanically or chemically emulsified oil**, but may require pre-filtration or pre-separation. Microfiltration works best with non-silicated cleaners.

Pollution Prevention

Extending the Life of Aqueous Cleaning Solutions

The book "Pollution Prevention and Control Technology for Plating Operations" provides an example of return on investment for a microfiltration system. The bath volume was 2400 gallons, and the cleaner cost was $0.42/gallon. Equipment and installation costs were $27,000, and operating costs were $6,250/year. Total savings were $18,715. The return on investment was 2.1 years (Cushnie, 1994).

One of the most significant concerns regarding the use of membrane technologies is that some components of the cleaning solution may be removed along with the contaminants. If this happens, chemicals will have to be added to the bath before it can be reused.

Case Studies

Ultrafiltration

An Illinois manufacturer of painted steel shelving units cleans metal surfaces prior to painting to remove mill oils and metalworking fluids. Parts are cleaned and phosphated in a 5000 gallon heated, aqueous immersion tank, using nonionic surfactants, and rinsed with a fresh water spray. The pH of the bath is maintained at 3.5 and the concentration of the cleaner is checked regularly (the cleaner contains both surfactants and phosphates).

Although the change to this aqueous system eliminated some issues associated with the previously used trichloroethylene degreasing tank, oil buildup in the cleaner and rinse tank were unacceptable. The bath had to be disposed of approximately every three to four months because of poor product quality. The spent bath was classified as a hazardous waste, and was incinerated off-site in a cement kiln. Management costs for transportation and incineration totaled approximately $15,000 annually.

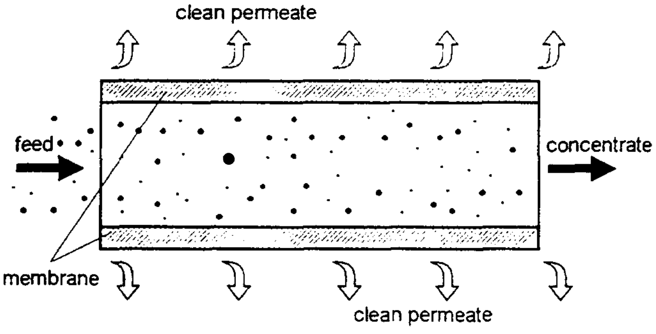

Figure 2: Crossflow membrane filtration (Prosys Corporation, 1992)

With the assistance of the Hazardous Waste Research and Information Center, Illinois, the company tested and installed an ultrafiltration unit. Primary objectives were to reduce waste and to preserve product quality.

The ultrafiltration process preferentially removed surfactants from the cleaning solution. However, simply adding additional chemical solution would have resulted in excessively high phosphate concentrations. The company resolved the issue by adding a neutral cleaning additive that contained the surfactant component in the original cleaner.

Although the ultrafiltration system did require significant capital investment, savings were achieved through reduced raw materials usage, plant down time, and waste disposal costs. Ultrafiltration has extended the bath life to over 3.5 years. The payback period was 6.9 months, the net present value was $152,143, and the interest rate of return was 178 percent (Lindsey et all. 1994).

Microfiltration

An Ohio company that fabricates commercial aluminum cookware uses aqueous cleaning followed by a deionized rinse to remove machine oil, kerosene and dirt from parts prior to hard anodizing. This system originally resulted in wastewater with up to 150 milligrams per liter of oil and grease, exceeding local regulatory limits of five milligrams per liter for both oil and grease and kerosene.

A microfiltration system was installed to remove these contaminants. The resulting solution could be discharged under current limits. Even better, contaminants are sufficiently removed for the water to be reused for cleaning.

The system, which allows 99 percent of water to be reused, had a payback period of less than three months, based on the cost of off-site disposal (EPOC, date unknown).

Conclusion

If you have decided that your aqueous cleaning bath is not accomplishing all you had hoped for, either environmentally or economically, it is not too late to consider options to maximize the bath life or to recycle the bath. Keep in mind that the more chemical emulsifying power your cleaner has, the harder it will be to remove the contaminants later. You may want to consider switching to a cleaner with less cleaning ability, and relying more on physical mechanisms such as agitation, sprays and ultrasonics to remove oil and other contaminants.

If you are in the market for a new aqueous cleaning system, consider recycling alternatives at the same time.

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August 18, 1994, telephone conversation with Jim Kavanagh, Engineer, Licon, Inc. 914/477-0334. Another contact for Licon is John Campbell, Sales Representative.

August 18, 1994 telephone conversation with Tom Whalen, Sales Representative, U.S. Filter Corporation. 412/772-0044.

August 22, 1994, telephone conversation with Scott Striker, District Manager, Osmotics. 800/848-1750.

August 25, 1994 telephone conversation with Ed Smiley, PhaSep, 704/867-2651.

Vendors

Alfa Laval Separation, Inc.
955 Mearns Road
Warminter, PA 18974
215/443-4030
(ultrafiltration, filtration)

Aqualogic
20 Devine Street
North Haven, CT
203/288-4308
(ultrafiltration.)

Atotech
2 Riverview Drive
P.O. Box 6768
Somerset, NJ 08875
1/800/PLATING
(filtration)

Baker Brothers Systems
44 Campanilli Parkway
Stoughton,MA 02072
617/344-1700
(filtration)

DJM Industrial
10440 Travis St.
Walton, KY 41094
(ultrafiltration, filtration)

EPOC Filtration and
Separation Systems
3065 North Sunnyside
Fresno, CA 93727
290/291-4926
(separation, membrane
technology)

Hawken Technologies
463 Turner Drive, Unit 103
Durango, CO 81301
303/247-4655
(ultrafiltration)

Hyde Product, Inc.
28045 Ranney Parkway
Cleveland, OH 44145-1188
216/871-1188
Fax 216/871-1143
(ultrafiltration, separation)

Industrial Filter
5900 West Ogden Avenue
Cicero, IL 60650
708/656-7800
(filtration)

Ionics, Inc.
65 Grove Street
Watertown, MA 02172
617/926-2500
(filtration)

Iverson Industries
9799 Princeton-Glendale
Cincinnati, OH 45246
(filtration)

Jarvis Manufacturing
125 Space Park South
Nashville, TN 37211
615/781-3093
(filtration)

JWI
2155 112th Avenue
Holland, MI 49424
616/772-9011
(filtration)

Kinetico Engineered Systems
10845 Kinsman Road
Newbury, OH 44065
216/564-5397
(ultrafiltration, filtration)

Kock Membrane
Systems, Inc.
850 Main Street
Wilmington, MA 01887
1/800/343-0499
(ultrafiltration)

Komline-Sanderson
12 Holland Avenue
P.O. Box 257
Peapack, NJ 07977
908/234-1000
(ultrafiltration, filtration)

Membrex, Inc.
155 Route 46 West
Fairfield, NJ 07004
201/575-8388
(separation, ultrafiltration)

Memtek
28 Cook Street
Bilerica, MA 01821
508/667-2828
(filtration)

Met-Pro Systems
160 Cassell Road
Harleysville, PA 19438
(filtration)

Met-Pro / Sethco
Hauppauge, NY
516/435-0530
(filtration)

Napco, Inc.
Plymouth Industrial
Napco Drive
Terryville, CT 06786
203/589-7800
(filtration)

Osmonics
5951 Clearwater Drive
Minnetonka, MN 55343
1/800/438-6766
(ultrafiltration, filtration, separation)

Pasco
Byrne Building
Lincoln and Morgan
Phoenixville, PA 19460
215/983-9585
(filtration)

Penfield Liquid Treatment
Systems
8 West Street
Plantsville, CT 06479
203/621-9141
(ultrafiltration)

PhaSep
1111 Jenkins Rd.
Gastonia, NC 28052
704/867-2651
(separation)

ProSys Corporation
187 Billerica Road
Chelmsford, MA 01824
508/250-4940
(ultrafiltration)

Sanborn
Wrentham, MA
1/800/343-3381
(ultrafiltration)

SERFILCO
1777 Shermer Road
Northbrook, IL 60062
1/800/323-5431
(ultrafiltration, filtration)

U.S. Filter Corporation
181 Thorn Hill Road
Warrendale, PA 15068
412/772-0044
(filtration)

This is the thirty-first in a series of fact sheets Ohio EPA has prepared on pollution prevention. For more information, call the Office of Pollution Prevention at 614/644-3469.

The Office of Pollution Prevention was created to encourage multi-media pollution prevention activities within the state of Ohio, including source reduction and environmentally sound recycling practices. The office analyzes, develops and publicizes information and data related to pollution prevention. Additionally, the office increases awareness of pollution prevention opportunities through education, outreach and technical assistance programs directed toward business, government and the public.

United States
Environmental Protection
Agency

Office of Research and
Development
Washington DC 20460

EPA/625/R-93/015
February 1994

EPA

Guide to Cleaner Technologies

Organic Coating Removal

Available Cleaner Technologies for Coating Removal: Descriptive Aspects and Operational Aspects

Table 1. Available Cleaner Technologies for Coating Removal: Descriptive Aspects

Technology/ Coating Removal Mechanism	Pollution Prevention Benefits	Reported Application	Benefits	Limitations
Plastic Media Blasting Impact/ Abrasive	• Eliminates VOCs and HAPs • Uses nontoxic media • Uses a dry process • Spent media are cleaned and reused several times for paint stripping • Some spent thermoplastic media are recyclable to make plastic products	• Removes paint from a variety of metal and non-metal substrates • Strips aircraft components and ground support equipment • Cleans/strips commercial and industrial parts • Removes powder coatings from sensitive substrates	• Provides high-throughput-controlled coating removal • Can selectively remove individual coating layers • Eliminates water use • When stripping is done with thermoplastic media, the waste may be recyclable	• Spent plastic media contain paint chips and so may be hazardous waste • Requires workers to wear respiratory and eye protection equipment • Blasting generates high noise levels • May cause metal substrate damage • More aggressive media types damage fiberglass or composite materials • Contaminants in media cause stress risers in the substrate • Uses flammable media
Wheat Starch Blasting Impact/ Abrasive	• Eliminates VOCs and HAPs • Spent media are cleaned and reused several times for paint stripping • Uses a nontoxic, biodegradable medium • Uses a dry process	• Gentle stripping action suitable for abrasion sensitive fillers and composite materials • Gaining acceptance for thin, soft aluminum in commercial aircraft skins	• Provides controlled coating removal • Can selectively remove individual coating layers • Eliminates water use • Uses inexpensive media • Media are nontoxic and biodegradable	• Spent starch media contain paint chips and so may be hazardous waste • Dense contaminants in recycled media may damage substrate • Stripping rate is generally slow to moderate • Requires workers to wear respiratory and eye protection equipment • Blasting generates high noise levels • Media are moisture sensitive
Burnoff Coating Removal Thermal	• Eliminates VOCs and HAPs	• Removes thick coatings from a variety of coating line fixtures and tools	• Provides rapid removal of thick coatings • Can process complex shapes • Burnoff ovens can remove uncured coating	• Generates coating ash residue that may be hazardous waste • Will damage heat-sensitive materials such as heat-treated aluminum or magnets • Coatings containing halogens (PVC or PTFE) and/or nitrogen will produce corrosive offgas • Must not be used for low-melting metals or alloys • Must not be used with pyrophoric metals • May require offgas treatment, depending on local air permitting regulations • Potential for generation of products of incomplete combustion • Presents possibility of fire
Molten Salt Coating Removal Thermal	• Eliminates VOCs and HAPs	• Removes thick coatings from a variety of coating line fixtures and tools	• Provides rapid removal of thick coatings • Can process complex shapes • Salt bath ensures even heating • Rinsewater waste is compatible with conventional water treatment systems	• Generates by-product sludge that may be hazardous waste • Will damage heat-sensitive materials such as heat-treated aluminum or magnets • Must not be used for low-melting alloys • Must not be used with pyrophoric metals • May require offgas treatment, depending on local air permitting regulations • Potential for generation of products of incomplete combustion

(continued)

Table 1. (Continued)

Technology/ Coating Removal Mechanism	Pollution Prevention Benefits	Reported Application	Benefits	Limitations
Sodium Bicarbonate Wet Blasting Abrasive/ Impact	• Eliminates VOCs and HAPs • Uses nontoxic media	• Removes paints from a variety of metal substrates • Depaints wood without damaging the substrate • Cleans and depaints brick walls • Removes heavy accumulations of grease and dirt from mechanical equipment	• Provides a controllable process for coating removal • Can selectively remove individual coating layers • Uses inexpensive stripping media • In some cases, liquid waste may be discharged to a conventional wastewater treatment plant • Use of water dissipates heat generated by the abrasion • Eliminates need to prewash surface • Sodium bicarbonate wastestreams are generally compatible with existing water treatment systems	• Uses nonrecyclable stripping media • Generates wet sodium bicarbonate sludge containing coating debris, which may be a hazardous waste • System must be available to collect and treat wastewater containing sodium bicarbonate and paint chips • May require exhaust ventilation system to control particulate • Requires workers to wear respiratory and eye protection equipment • Blasting generates high noise levels • Media can be aggressive so potential for substrate damage exists
Carbon Dioxide Pellet Cryogenic Blasting Cryogenic/ Abrasive/ Impact	• Eliminates VOCs and HAPs • Uses a dry process so no wastewater is generated • Coating chips collected dry with no media • Uses natural or industrial sources so no net production of carbon dioxide occurs	• Strips surfaces needing high degree of final cleanliness • Useful for equipment where it is desirable to avoid disassembly • Useful when volume of residue must be minimized such as with radioactive-contaminated components or coatings containing hazardous metals (e.g., cadmium or lead)	• Generates low volume of dry waste (none from the media) • Eliminates water use • Provides well-defined coating removal pattern • Can selectively remove individual coating layers • Requires limited pre- or poststripping cleanup • No masking needed except for delicate materials such as soft clear plastics • Equipment can be stripped without disassembly • No media separation/ recycling system needed • No media disposal cost • Pellets driven into interstitial spaces vaporize, leaving no residue	• Generates small volume of coating debris, which may be a hazardous waste • Requires ventilation to avoid potentially dangerous CO_2 concentrations • Generates airborne particulates that may contain metal from the coatings • Requires workers to wear respiratory and eye protection equipment • Requires workers to wear hearing protection • Possible worker exposure to extreme cold • Potential for worker injury from high-velocity CO_2 pellet impact • Rebounding pellets may carry coating debris and contaminate the work area or workers • Nonautomated system fatigues workers quickly • Possible static electricity buildup on substrate if no grounding provided • Some coating debris may redeposit on substrate • Low temperatures can cause condensation on substrate • Large local temperature drops can occur in substrate but confined mainly to the surface layer • May damage thermoset composite materials • Difficult to control coating removal on graphite-epoxy composites • Slow coating removal rate • Equipment bulky and capital intensive

(continued)

Table 1. (Continued)

Technology/ Coating Removal Mechanism	Pollution Prevention Benefits	Reported Application	Benefits	Limitations
High-Pressure Water Blasting Impact	• Eliminates HAPs and VOCs • Water can be processed and recycled during stripping, reducing wastewater volume	• Robotic systems for rapid coating removal	• High stripping rate • Stripping water can be recycled • Wastewater stream is compatible with existing water treatment systems	• Coating debris sludge may be hazardous waste • System is needed to collect and recycle stripping water • Ultrahigh-pressure systems (>15,000 psi) require expensive robotic operation • Misapplied water jet will damage substrate • Blasting generates high noise levels • Water can enter cavities • Water can penetrate and/or damage joints, seals, and bonded areas
Medium-Pressure Water Blasting Impact/may be supplemented with softening agents or abrasives	• Eliminates HAPs; some systems use VOCs containing softeners • Water can be processed and recycled during stripping reducing wastewater volume	• Rapid coating removal	• High stripping rate • Stripping water can be recycled • Wastewater stream is compatible with existing water treatment systems	• Coating debris sludge may be hazardous waste • System is needed to collect and recycle stripping water • Requires workers to wear respiratory and eye protection equipment • Blasting generates high noise levels • Mechanized applications typical due to high reaction forces • Misapplied water jet will damage substrate • Water can enter cavities • Water can penetrate and/or damage joints, seals, and bonded areas
Liquid Nitrogen Cryogenic Blasting Impact	• Eliminates HAPs and VOCs • Uses a dry process • No dust, fumes, or chemicals released • Coating chips collected dry with small volume of media	• Removes thick coatings of coating from a variety of coating line fixtures and tools	• Environmentally clean • No ash residue • Low waste volume • Eliminates water rinse • Very fast cycle times (5 to 15 min) give high throughput rate • Works well on thick coating buildups	• Generates some solid waste containing coating chips and spent plastic media, which may be a hazardous waste • May require ventilation system to prevent nitrogen buildup in confined spaces • Requires worker protection from low temperatures during unloading • Not effective on thin coating films • Less effective on epoxies and urethanes • Existing technology limits part size to less than 6 ft tall and 38 in diameter weight less than 400 lb per stripping cycle

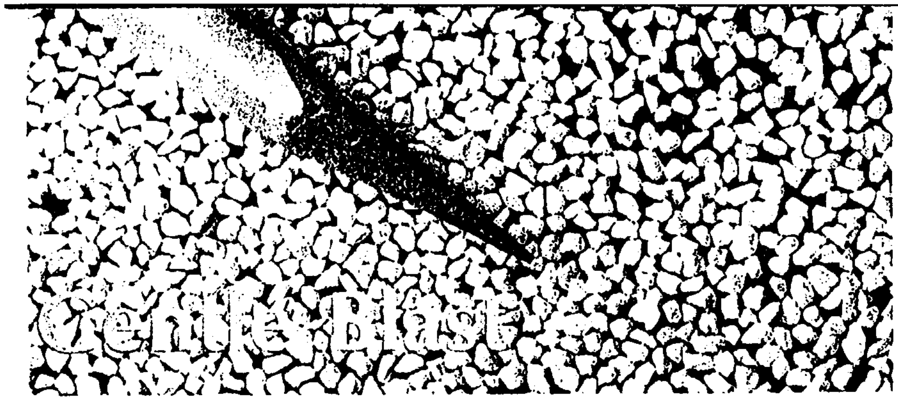
Table 2. Available Cleaner Technologies for Coating Removal: Operational Aspects

Available Technology Type	Process Complexity/ Required Skill Level	Waste Products and Emissions	Capital Cost	Energy Use	Operations Needed After Stripping	References
Plastic Media Blasting	Medium/ Medium	• Solid coating residue and spent media waste • Airborne particulates • Noise	Medium	• Compressed air to propel blasting media • Energy for media recovery and recycle, dust collection, and ventilation	• Continuous separation of media from stripped coating particles and spent media during stripping • Remove masking • Dispose of spent media and contained coating residue waste • Some spent thermoplastic media (even with coating residue) can be reused to make plastic parts	Abbott, 1992 Bailey, 1992 Baker, 1991 Bowers-Irons et al., 1991 Capron and Wells, 1990 Composition Materials Co., 1993 Cundiff et al., 1989 Dicaire, 1990 Galliher, 1989 Groshart, 1988 *HazTECH News*, 1991 Lyons, 1990 Novak, 1990 Pauli, 1989 Roberts, 1989 U.S. DoD, 1988 U.S. Navy, 1987 U.S. Technology Corporation, 1993 Wasson and Pauli, 1993
Wheat Starch Blasting	Medium/ Medium	• Solid coating residue and spent media waste • Airborne particulates • Noise	Medium	• Compressed air to propel blasting media • Energy for media recovery and recycle, dust collection, and ventilation	• Continuous collection and reuse of spent media during stripping • Remove masking • Dispose of spent media and contained coating residue waste • Spent media can be treated by biodegradation	Drake, 1993 Larson, 1990 Lenz, 1991 Oestreich and Porter, 1992 Oestreich and Waugh, 1993
Burnoff Coating Removal	Low/ • Low for operation • High for maintenance	• Ash • Offgas	Medium	• Electricity or gas supply for heating	• Cool down • Ash removal and collection	Coberth and Ceyssons, 1993 Izzo, 1989 Mann, 1991 *Metal Finishing*, 1990 Whelan, 1993
Molten Salt Coating Removal	Low/ • Low for operation • High for maintenance	• Salt/coating by-product sludge • Offgas • Rinse water	Medium	• Electricity or gas supply for heating	• Cool down • Water rinse	Gat et al., 1993 Malloy, 1993 *Metal Finishing*, 1990
Sodium Bicarbonate Wet Blasting	Medium/ Medium	• Liquid waste containing coating residue and spent media • Some airborne particulates • Noise	Low	• Compressed air and water supply to propel blasting media • Ventilation to control particulate	• Remove masking • Dispose of sodium bicarbonate solution and coating residue waste	Chen and Olfenbuttel, 1993 Kline, 1991 Larson, 1990 Peebles et al., 1990 Spears, 1989 Svejkovsky, 1991 Wasson and Haas, 1990

(continued)

Table 2. (Continued)

Available Technology Type	Process Complexity/ Required Skill Level	Waste Products and Emissions	Capital Cost	Energy Use	Operations Needed After Stripping	References
Carbon Dioxide Pellet Cryogenic Blasting	Medium/ Medium	• Solid coating residue waste • Airborne particulates • CO_2 gas • Noise	Medium	• Liquid carbon dioxide supply • Compressed air supply to propel blasting media	• Remove masking • Dispose of coating residue waste	APCI, 1984b Boyce et al., 1990 Burcham, 1993 Cheney and Kopf, 1990 Cold Jet, Inc., 1989 Cundiff and Matalis, 1990 Foster et al., 1992 Ivey, 1990 Kopf and Cheney, 1989 Larson, 1990 Schmitz, 1990 Svejkovsky, 1991 Wolff, 1984
High-Pressure Water Blasting	High/ • Low for operation • High for maintenance	• Sludge waste containing paint residue • Wastewater • Some airborne particulates • Noise	High	• Electricity to drive water pump	• Remove masking • Dispose of coating residue sludge and wastewater	Hofacker et al., 1993 Howlett and Dupuy, 1993 Stone, 1993 U.S. Army, 1992
Medium-Pressure Water Blasting	Low/ High	• Sludge waste containing paint residue (and in some systems solvent or abrasive additives) • Wastewater • Some airborne particulates • Noise	Low	• Electricity to drive water pump	• Remove masking • Dispose of coating residue sludge and wastewater • If used, dispose of abrasive or sorbent or other treatment medium carrying solvent	Bailey, 1992 Boeing, 1993 Howlett and Dupuy, 1993 *New Scientist*, 1990 Petkas, 1993
Liquid Nitrogen Cryogenic Blasting	Medium/ • Low for operation • High for maintenance	• Solid coating residue and spent media waste • Inert nitrogen gas	Medium	• Liquid nitrogen supply	• Vent nitrogen gas from the stripping cabinet • Allow parts to warm for 5 minutes • Dispose of coating residue waste	APCI, 1982, 1984a, 1984b, 1985 Mathur, undated *Products Finishing*, 1983 Stroup, 1991 Wolff, 1984



Plastic blast media removes paint and surface soils without harming substrates...

By Joseph E. Konopka
General Manager
Aero-Blast Products, Inc.
South Bend, Indiana

Just when you thought you knew all there was to know about blast cleaning, along comes a new twist in the technology.

In the past, new ideas in blasting technology have come in the form of innovations such as steel shot, the wheel-blast process, wet or vapor blasting, glass-bead and closed-cycle blasting.

Now there may be a new "mover and shaker" in refinishing and surface preparation processes—granulated thermoset plastic media.

Plastic media has been used in other industrial-blasting applications. Polycarbonate for deburring and rubber deflashing, and granulated plastics for electronics deflashing, as examples.

But the newest twist in abrasive blasting is the use of plastic media for paint and coating removal and for surface preparation.

Chemical-Strip Replacement. The idea of using plastic media for paint removal came about in 1979 when the U.S. Air Force began looking for alternatives to chemical stripping of paint from aircraft. Facing an EPA-imposed goal of reducing toxic wastes and disposal of them at military facilities, engineers at Hill Air Force Base in Ogden, Utah began looking for alternatives.

The Air Force looked into a wide variety of stripping processes, including dry blast with organic medias, plastics, dry ice, and conventional abrasives; flash lamp; and laser. Preliminary testing showed the viability of plastic-media blasting.

Dry blasting with granulated plastic pellets ultimately was shown to be an immediate, off-the-shelf, economical alternative to chemical stripping.

Now Stripping Aircraft. While still a nascent process, "dry" stripping of aircraft is being done by the Air Force (on the F-4 fighter); by the U.S. Army (on helicopters at Corpus Christi Army Depot); by Boeing-Vertol (on the Army's Chinook helicopters); and by the Coast Guard, at Elizabeth City, North Carolina.

Among airlines, the largest commercial carrier to utilize the process is Northwest Airlines in Atlanta, Georgia. Here an entire DC-9 is typically dry stripped in ten hours by a five-man crew.

Stripping Rejects. The potential for industrial refinishing operations became apparent when the aviation industry began using plastic abrasives to dry strip components such as propellers, wheels, brake parts, seat frames and numerous other parts that have to be stripped prior to structural testing. As Table I indicates, a ten to one time ratio exists between chemical stripping and plastic-media blast cleaning in many applications.

To date, there are only a few industrial users of plastic media for depainting processes. But the potential has been clearly shown in early testing and demonstrations. And there certainly is a need for an efficient, non-toxic process for stripping paint from rejects in products-finishing plants.

Dry blast stripping with plastic media rapidly and safely removes paint from glass headlight lenses; from cast aluminum automobile-mirror frames; from glass-reinforced nylon steering column housings; from fiberglass au-

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TABLE I
Chemical Vs. Dry Plastic Blast: F-4 Aircraft Parts

Component	Cleaning Time Minutes (Chemical)	Cleaning Time Minutes (Drystrip)
Rudder	216	16
Inboard Leading Edge Flap	168	22
Spoiler	40	14
Outboard Leading Edge Flap	168	19
Aileron	388	32
Wingfold	525	54
Stabilator	589	55

tomobile bodies (Corvettes); and from thin steel space heater cabinets—all without causing excess pitting, etching, or metal-expansion damage.

More remarkable yet is that coatings can generally be removed without removing protective underlying coatings such as Alclad, anodize, or in many cases, even the primer.

Easy on Substrate. How is it possible to strip such delicate materials without excessive etching of or damage to the substrate? Part of the answer is in the low density of the plastic media (Table II), which ranges from approximately 1.15 to 1.5 gm/cc. This low density allows blasting at low nozzle pressures, typically 30-60 psi in pressure blast systems.

The media is available in three hardnesses, ranging from three to four on the Mohs scale. Such hardness values are higher than those of most coatings, but not hard enough to damage most delicate substrates, when working within recommended parameters.

Adjusting the media type (hardness), the particle size and the air pressure allows good control of stripping.

Wet Blast. Are there other potential applications in industrial blasting? Yes. Plastic media can be used in wet-blast or vapor-blast processes, including depainting, cleaning and surface roughening. The plastic will not absorb much water and will not decompose in wet blasting.

Paint Hooks/Racks? Can plastic media be used to clean paint hooks, trays, and racks used in production painting? Probably not. These items are sometimes too heavily coated to be stripped efficiently with plastic media. However, plastic media is quite suitable for removing the carbon residue remaining after removal of built-up paint by burn-off.

Surface Prep. There is also potential for plastic-media blasting in surface preparation. It may be substituted for hand or disc sanding in some cases. This works well on plastic components such as the urethane bumper fascias on new automobiles.

TABLE II
Plastic Blast Media Properties

Property	Plastic Media				
	Type A	Type B	Type C	Walnut Shell	Glass Beads
Density (gms/cc)	1.15	1.5	1.5	1.3	2.5
Hardness (Moh)	3 –	3.5	4	3	5.5
Impact Strength Scale (1 to 10)	4 +	6	7 +	4	2
Moisture Content	<0.1%	<0.1%	<0.1%	10% (Variable)	0%
Water Absorption (24 hrs. 25 °C)	0.13%	0.5%	0.25%	100%	0%
Explosibility Index	5	.2	<.2	10	0
Ignition Temp. (°C)	440	530	>530	430	N.A.
Min. Explosive Conc. (oz./ft³)	.045	.085	.09	.040	N.A.
Chemical Nature	Inert	Inert	Inert	Degradeable	Inert

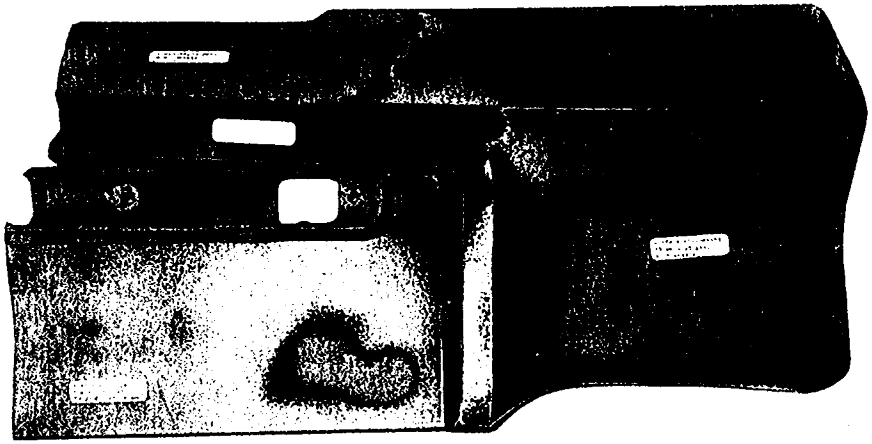
NOTES: Hardness (Moh Scale): Talc = 1 Diamond = 10
Impact Strength: Relative scale of comparison with 10 being strongest and 1 the most friable.
N.A.: Not Applicable

Partial stripping or "scuffing" of components is another efficient way to use plastic media. Fine grades of granulated plastic can quickly take the "sheen" off coatings without pitting or scarring the surface.

With laminated composites becoming more common, plastic media fills the need for a media tough enough to roughen delicate surfaces prior to bonding, without lifting underlying fibers. The same advantage holds for surface preparation on plastics, ceramics, fiberglass and other fiber-reinforced plastics.

Recycling. The cost of plastic media requires it to be recycled to be truly cost-effective as a blast-cleaning media. Granulated plastic pellets are very durable at pressures below 50 psi (nozzle pressure), having an average break-down rate well under ten pct per cycle. Thus reclamation is practical and this does reduce the cost of media.

Recycling of plastic media is usually not a problem when a blast cabinet is used. However, when the applica-



LAYER-BY-LAYER stripping of paint from urethane bumper section. Copper color is topcoat. Yellow, the undercoat. Black is primer. Light brown, the urethane plastic substrate.

tion dictates open blasting, special reclamation/exhaust equipment may be needed.

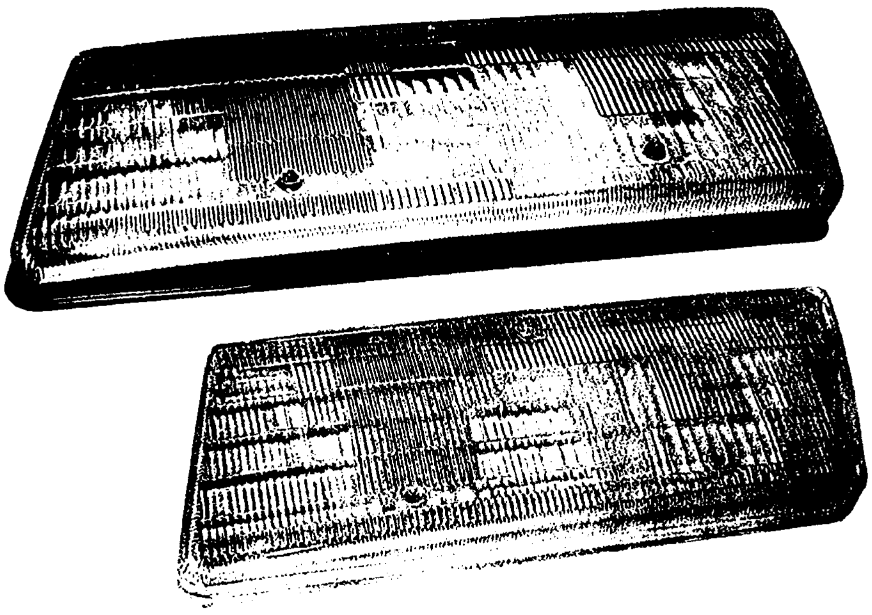
An efficient method of reclaiming and cleaning plastic media is to use an adjustable air cyclone, followed by a vibrating screen to remove larger contaminants. An appropriately designed cyclone will differentiate between the lightweight plastic granules and the pulverized paint and media dust. The resultant dust can be vacuumed simultaneously into the dust collector.

Separation of media from dirt and dust is important, since dust in the recycled media can act as a buffer, interfering with the impacting particles and hampering visibility.

While the media continually refractures to provide fresh cutting edges, it loses its efficiency as a paint stripper at particle sizes smaller than 80 mesh. Thus a well-designed system will begin removing these useless particles, allowing "fresh" media to be added periodically to the original load rather than totally disposing of a media batch at one time.

Additionally, an in-line magnetic separator can remove ferrous materials.

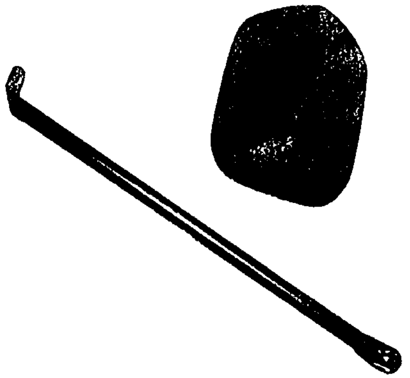
While traditional suction-blast cabinets can utilize plastic media, it is difficult to achieve efficient particle velocity and smooth media flow in using such equipment. Also, the dust collectors on some suction-blast cabinets may extract excess reusable plastic media while being inefficient in the separation and removal of contamination and dust. Pressure-blast systems are recommended where high production is required.



BEFORE AND AFTER. At top, a headlamp lens with black trim. Plastic blast media removed the trim paint without pitting, etching, fogging or cracking the lens.

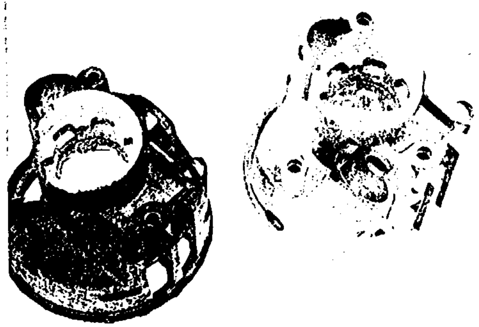
Because of the plastic media's high angle of repose, steep-cone bottoms are recommended for pressure pots and hoppers. An aeration device at the bottom of the pressure pot can aid the feed of media into the air flow. Equipment incorporating these special features is now commercially available.

Leftovers. Disposal of the residual dust should be done according to EPA guidelines. However, the dispersion of these elements in the dry residual dust may be so minimal that the waste may not be considered toxic according to existing guidelines. You



POWDER COATING was removed from mirror-frame components in less than 30 sec.

RUNS AND SAGS on painted housing at left have been removed (center) by dry-blast plastic media, leaving the rest of the part surface-prepped for refinishing. At right coating has been removed from glass-reinforced nylon.

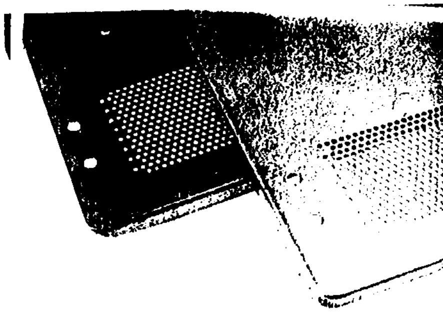


COMPLEX cast aluminum part shown in this photograph was cleaned in less than a minute.

should analyze all wastes and check with your local, state and national authorities.

Since the coatings being removed may contain trace amounts of lead, chromium, and other heavy metals and toxic agents, operators should be adequately protected.

Severe Corrosion. The advantage provided by plastic media in its low-abrasiveness becomes a shortcoming when the goal is to remove severe corrosion. The plastic is simply not aggressive enough to clean out corrosion pits in ferrous metal surfaces. But it will remove light rust and is often effective on filiform corrosion in aluminum.



PERFORATED panel from room heater was cleaned in less than 20 sec, without etching the surface.

DRY STRIPPING a DC-9 at Northwest Airlines.

Masking. Some soft substrates may be undesirably marred by overspray from a plastic-media-blast operation. Therefore, masking may be recommended for certain applications. Ordinary duct tape is effective. For more protection, a rubber-backed sandblast stencil tape will provide better masking.

Unwanted intrusion of plastic media and dust into a part cavity can be prevented by stuffing gaps with plastic sheeting, special plugs, or filling with butyl rubber caulk.

Use Your Imagination! With sophisticated new coating materials creating finishing and refinishing problems, there is now another way to remove coatings that are difficult to remove by other means. The potential for granulated plastic media in dry or wet blast stripping and surface preparation is substantial. It requires only the imagination of production engineers, foremen, and management to envision applications.

As a national credit card promotion suggests, master the possibilities!

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Industrial
Innovations
FOR TOMORROW
Advances in Industrial
Energy-Efficiency Technologies

Supercritical CO_2—an Environmentally Acceptable Alternative for Industrial Cleaning Applications

Alternative cleaning technologies are needed to help industry comply with the international phaseout of CFCs.

Chlorofluorocarbons (CFCs) have been used by industry for decades to clean organic and particulate contaminants from metals, plastics, composites, ceramics, electronic components, and other materials. CFCs are suspected of depleting the stratospheric ozone layer, which prevents damaging solar ultraviolet radiation from reaching the earth's surface. Because of the environmental implications of continued use of CFCs, the United States has joined other nations in calling for a halt to CFC production by the end of the century.

The CFC phaseout has spawned the development of a number of alternative cleaning technologies to meet the needs of industry. Although several solvents have been identified as substitutes for CFCs, they appear unable to accomplish the "precision cleaning" required in applications prevalent in the computer, aerospace, and medical industries. Additionally, they carry environmental hazards of their own.

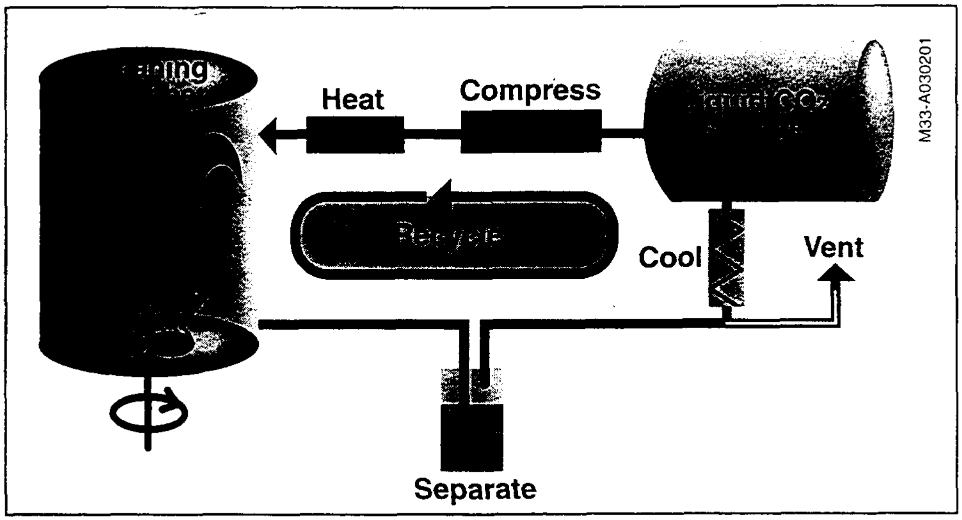
The supercritical CO_2 cleaning system shown here uses heat and pressure to create liquid CO_2 that cleans contaminants from a variety of components. The inset photo shows the system's working chamber. (Photos courtesy of Los Alamos National Laboratory)

One new technology—supercritical fluid cleaning—has been identified as a viable, environmentally benign precision cleaning technology. Three national laboratories have joined four industrial partners and the Industrial Waste Reduction Program in the U.S. Department of Energy's Office of Industrial Technologies to form the Joint Association for the Advancement of Supercritical Technology (JAAST).

The JAAST program is addressing the technical challenges of developing supercritical fluid systems and is working toward commercializing a specific technology—supercritical carbon dioxide (CO_2) cleaning—for use in government and industrial installations. To this end, JAAST members are developing the necessary data to measure the applicability of supercritical cleaning and to evaluate its economic feasibility.

The joint government/industry group is investigating supercritical CO_2 cleaning for a number of applications.

In a supercritical CO_2 cleaning system, the components to be cleaned are placed inside a chamber. Liquid CO_2 is compressed and heated; the CO_2 becomes supercritical at a



Supercritical CO_2 is pumped into a chamber where it cleans components; the CO_2 exiting the chamber is expanded into a gas, and the contaminants are separated out.

temperature of 89°F (31.7°C) and pressure of 1095 psi (7548 kPa). Beyond this point, the gas and liquid phases of the CO_2 are indistinguishable. The supercritical fluid is pumped into the chamber where it cleans the component. The CO_2 exiting the chamber is allowed to expand into a gas, and the contaminants are separated out. The gaseous CO_2 is then either vented or cooled and condensed into a liquid, which is recycled back into the system.

The members of JAAST work in close coordination. The national laboratories—Los Alamos, Sandia, and Pacific Northwest (PNL)—are conducting the basic research. Hughes Aircraft Company, Boeing Aerospace and Electronics Engineering, and IBM are supplying the parts to be cleaned and ancillary research; Autoclave Engineers is supplying the cleaning equipment.

Research at Boeing is currently focusing on cleaning printed wire boards. For this project, supercritical CO_2 cleaning will take place at Los Alamos, initially on a small scale. The goal is to determine optimal conditions for cleaning both organic and inorganic contaminants from the boards. Full-scale boards will then be tested in a SuperScrub™ unit—a new, large-scale cleaning system recently developed by Autoclave Engineers.

Hughes Aircraft is conducting particulate removal studies and is evaluating recycling the CO_2 solvent during the cleaning process. Hughes researchers are conducting these studies at Los Alamos, where special "clean" rooms are available for handling the test surfaces. The goal of the recycle evaluation effort is to determine the degree of cleanliness of the CO_2 required for reuse. Hughes is also studying other supercritical fluids that may be viable in precision cleaning applications.

The other members of JAAST are involved in a variety of related projects. IBM is investigating the cleaning of organic, inorganic, and particulate materials from porous metal parts. Sandia is studying some of the physical and chemical processes involved in supercritical CO_2 cleaning. PNL researchers are performing bench-scale experiments using Boeing parts.

Supercritical CO_2 cleaning is both environmentally and economically attractive.

The environmental advantages alone of supercritical CO_2 cleaning over CFC-based cleaning are sufficient to make the new technology attractive. The majority of the approximately 100,000 tons (90,000 metric tons) of CFCs per year used for cleaning in the United States is eventually released to the atmosphere. This waste would be eliminated with the use of supercritical CO_2 cleaning. In addition, the oil used to produce CFCs would be saved.

A supercritical CO_2 cleaning system also has a number of economic advantages over a conventional cleaning system. The CO_2 system has a lower capital cost, requires less labor, can be installed in less space, and operates with a shorter batch cycle time. However, the principal economic advantage over CFCs is the estimated savings of hundreds of millions of dollars in solvent costs.

The JAAST program is expected to be completed by the end of 1994. Hughes Aircraft and Autoclave Engineers have already formed a venture partnership to market the technique. If the current projects prove successful, several other companies are planning to commercialize supercritical CO_2 cleaning equipment.

For More Information

Industrial Waste Reduction Program
EE-222
Office of Industrial Technologies
U.S. Department of Energy
1000 Independence Ave., SW
Washington, DC 20585
(202) 586-[illegible]

OFFICE OF INDUSTRIAL TECHNOLOGIES

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February 1994

EPA

Guide to Cleaner Technologies

Alternatives to Chlorinated Solvents for Cleaning and Degreasing

Available Technologies: Supercritical Fluids

Supercritical Fluids

Pollution Prevention Benefits

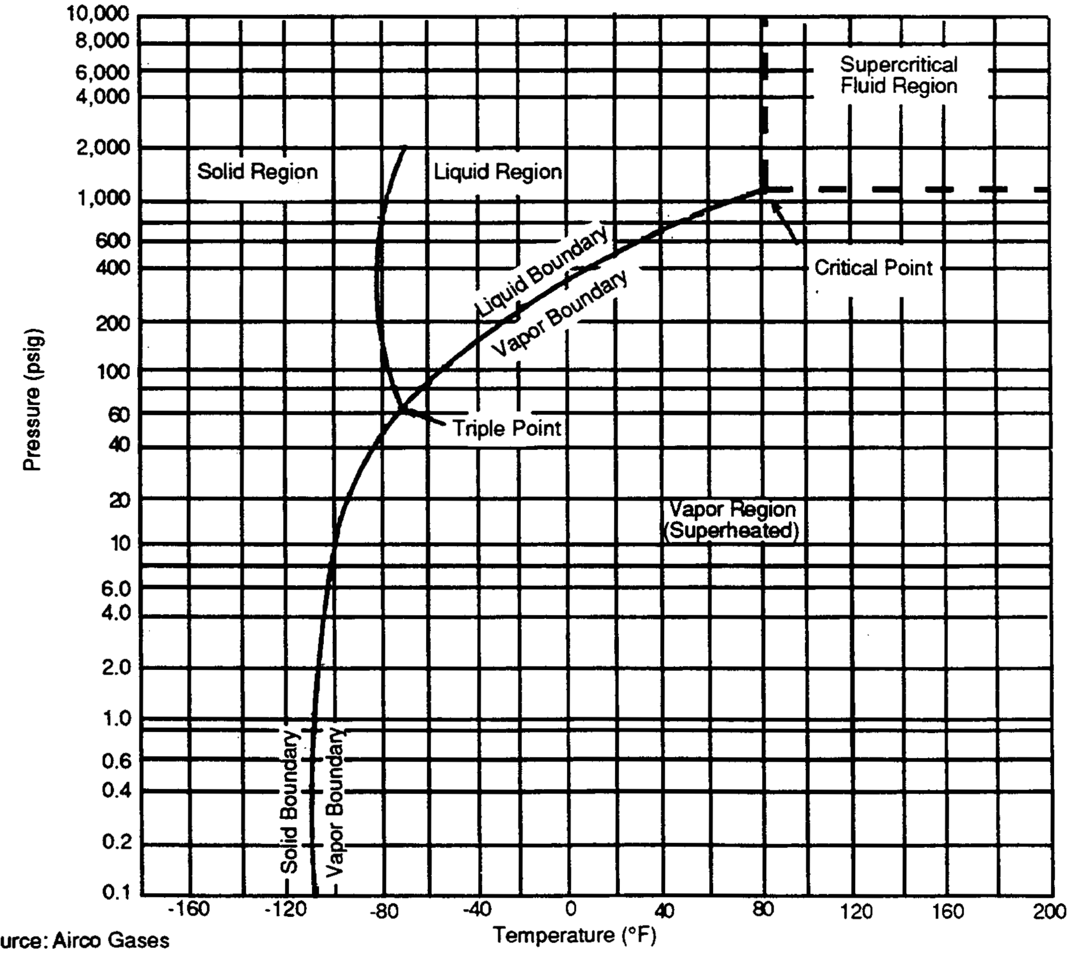
The main advantage of using carbon dioxide (CO_2) as a supercritical fluid (SCF) is that CO_2 is nonpolluting. CO_2 is derived from the atmosphere and is not created for use as a solvent. Furthermore, the small quantity of CO_2 released would have an insignificant effect on global warming. On the other hand, cosolvents, which may be used to improve the solvent power of CO_2, may have pollution potential and should be investigated before use. Energy is required to operate the pumps and temperature control equipment that are needed in supercritical cleaning equipment.

How Do They Work?

CO_2 compressed above its critical pressure (73.7 bars, or 1077 psi) becomes a critical fluid, and if also heated above its critical temperature (31.1°C, or 88.0°F), it becomes a supercritical fluid. Typically, however, the term *supercritical* (SC) is applied to any region in phase space that is above either the critical temperature (T_c) or the critical pressure (P_c). Critical and supercritical fluids are excellent solvents for dissolving many medium-molecular-weight, nonpolar or slightly polar organic compounds.

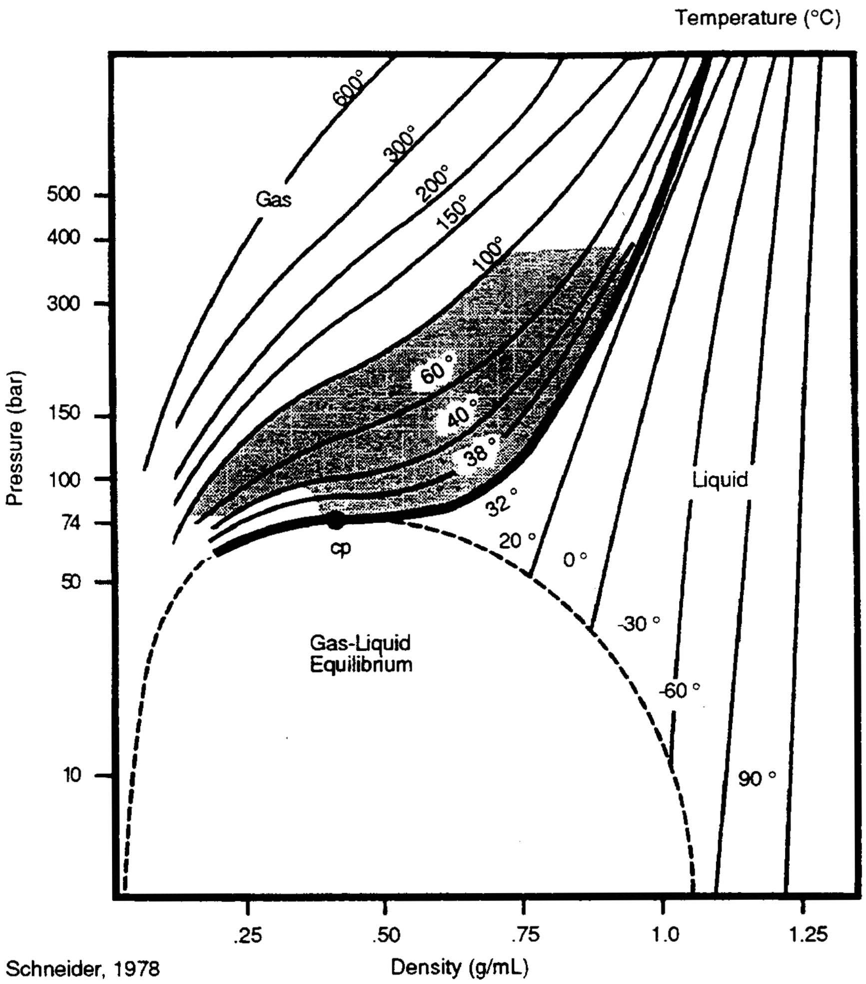
SCFs have more solvent power the denser they are.

Figure 1 is a phase diagram for CO_2 that shows its stable phase boundaries, including the supercritical region. The solvent power of supercritical fluids increases as the density of the fluid increases. The density of SC CO_2 can be made nearly liquid-like at moderate pressures. The shaded region in Figure 2 shows the pressure-temperature (*P-T*) region that is most useful for cleaning. Fluid densities range from approximately 0.2 to 0.8 g/cm^3. Figure 2 shows how the fluid density may be varied to achieve a broad range of solvating ability. It may be said that supercritical fluids can be "tailored" to achieve a desired solvent capability.



Source: Airco Gases

Figure 1. Phase diagram for pure CO_2.



Source: Schneider, 1978

Figure 2. Pressure-density diagram for pure CO_2; temperature in °C; cp = critical point.

Other factors that affect the cleaning abilities of SCFs are their gas-like low viscosity and high diffusivity, which enable them to penetrate into small confined spaces, such as cracks and blind holes. In the *P-T* region of interest (shaded area in Figure 2) viscosities are about twice those of the gas at atmospheric pressure and at the same temperature, whereas diffusivities are about 30 times smaller (Lira, 1988). However once CO_2 molecules have solvated contaminant molecules, the kinematic properties of the fluid may change, especially near the SCF/contaminant interface. With this change, the solvated contaminant species may be difficult to remove. In practice, some sort of mixing mechanism or flow control usually is built into the extraction vessel.

A typical SCF cleaning system consists of the following components:

- CO_2 source (compressed gas cylinder)
- Chiller to condense CO_2 gas to liquid
- Pressure pump to elevate CO_2 liquid pressure
- Hot water bath to elevate line temperature to that of the cleaning chamber
- Cleaning chamber where parts are cleaned
- Pressure reduction valve at fluid exit port
- Separator vessel to collect contaminants
- Air flow meter to monitor CO_2 usage.

Supercritical CO_2 dissolves and carries away soluble contaminants.

Samples to be cleaned are placed in the cleaning chamber, which also is called an *extraction vessel* or *autoclave*. The process is started by drawing CO_2 from the gas cylinder, then pressurizing and heating the CO_2 to the same *P-T* conditions as in the extraction vessel. Heat tape may be wound around all critical fluid transfer lines, and temperatures should be monitored at various points by thermocouples. SC CO_2 flows through the cleaning chamber where it dissolves and carries away soluble substances. After extraction, the

CO_2 and dissolved contaminants pass through a pressure reduction valve where pressure is dropped below P_c, and then they enter the separator vessel. As CO_2 returns to the gaseous state, its solvent power decreases substantially and contaminants drop out of solution and remain in the separator vessel. The CO_2 continues to flow out of the separator vessel through a flow meter and to the atmosphere.

As a rule of thumb, to achieve good solvency at moderate temperature, the fluid pressure should be 2 or more times the critical pressure of the fluid. Typical operating conditions for SCF cleaning equipment are listed in Table 7.

Table 7. Typical Operating Conditions for Supercritical CO_2 Cleaning

Parameter	Scientific Units	Engineering Units
Pressure (gauge)	100-300 bars	1,450-4,350 psi
Temperature	40-85°C	100-185°F
SC CO_2 Density	0.5-0.8 g/cm^3	30-50 lb/ft^3
SC CO_2 Flow Rate	1-5 kg/hr	2-11 lb/hr
Time	0.5-3 hours	0.5-3 hours

Operating Features

SCF cleaning exploits the marked improvement of the solvent power of CO_2 or other substances after they undergo a phase transition from a gas or liquid phase to become supercritical fluids. Supercritical CO_2 has been used very successfully to remove organic soils of moderate molecular weight and low polarity. Supercritical CO_2 does not give good results for soils that are ionic or polar in nature, such as fingerprints.

SCF cleaning is most useful for precision cleaning operations.

SCF cleaning is probably best reserved for removing small amounts of soil from parts that require a high degree of cleanliness. For example, precision cleaning operations have been performed successfully on the following devices: gyroscope parts, accelerometers, thermal switches, nuclear valve seals, electromechanical assemblies, polymeric containers, optical components, porous metals, and ceramics (Gallagher and Krukonis, 1991; Woodwell, 1993). The cleaning technology is available commercially.

Capital costs for installing SCF equipment are high, at least $100K for small-capacity equipment. The cost of the autoclave increases considerably with size. Small vessels may be only 1 liter in volume and are relatively inexpensive. Large vessels—30 liters, for example—are many times more expensive for the same pressure rating. If large parts are to be cleaned, it may be more cost effective to purchase lower-pressure-rated equipment and operate the SCF system for longer times at lower pressure. The expense of supplying CO_2 to the system, however, is quite small, about 7 cents per pound.

Application

Supercritical fluids have been used in organic chemical analysis equipment and in the food and flavor industries. SCFs have been used to clean and degrease precision parts in the defense industry since the mid-1980s.

Supercritical fluids have been used to remove machine coolants on aluminum and stainless steel substrates (Salerno, 1990). The cleaning process, performed at 35°C, 138 bars for 15 to 30 minutes, yielded a residual 0.65% of the coolants on the substrates. The solubility of the coolants ranged from about 1 to 5% under these conditions.

Benefits

Low viscosity and high diffusivity permit SCFs to clean within very small cracks and pore spaces. The solvent power of SCFs is pressure-dependent, making it possible to extract different soils selectively and precipitate them into collection vessels for analysis.

Limitations

Health and Safety. The only major safety concern is the danger of a pressure vessel or line rupture. However, the pressures used in SCF cleaning are well within the strength limits of most standard autoclave equipment.

Compatibility with Materials. SCFs are compatible with metals, ceramics, and polymers such as Teflon™, high-density polyethylene, epoxies, and polyimides. SCFs cause swelling in acrylates, styrene polymers, neoprene, polycarbonate, and urethanes (Gallagher and Krukonis, 1991). Components that are sensitive to high pressures and temperatures should not be cleaned by SCF methods. Process developments in the future probably will make SCF cleaning more aggressive toward removing cross-linked polymeric materials and displacing particulates.

Cleaning Efficacy. The major deficiencies of SCF cleaning are that SCFs are not effective in removing inorganic and polar organic soils, nor do they remove loose scale or other particulates. For these reasons, the soil must be well characterized to ensure its solubility in SCF before an investment is made in this technology.

It also is not known whether the process can remove a complex mixture of contaminants. Therefore, a detailed analysis of the contaminants must be done before the likelihood of success can be determined.

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Guide to Cleaner Technologies

Alternatives to Chlorinated Solvents for Cleaning and Degreasing

Available Technologies: Carbon Dioxide Snow

Carbon Dioxide Snow

Pollution Prevention Benefits

Chilled CO_2 is a nontoxic, inert gas that replaces solvent use to eliminate ozone-depleting substances. Because the CO_2 is recycled, there is no need for disposal, nor is any wastewater produced. It generates no hazardous emissions.

How Does It Work?

Gaseous or liquid CO_2 is drawn from a room-temperature gas cylinder or high-pressure dewar and expanded through a nozzle to produce fine CO_2 particles and CO_2 gas. These particles are dry ice *snowflakes* and are propelled by the gas stream.

The CO_2 gas or liquid is expanded through a special nozzle to form a jet. For example, when liquid CO_2 at 750 psi is throttled through a nozzle and expanded into a volume at 1 atm pressure, it undergoes a phase change to the solid state. The shape and size of the snowflakes depend on the configuration of the nozzle and the conditions in which the flake formed in the gas stream. The snowflakes can be individual crystals or collective groupings of crystallites.

Cleaning action is performed when the snow particles impact a contaminated surface, dislodge adherent contaminant particles, and carry them away in the gas stream. The process is effective in removing very small (submicron) particles, where fluid drag normally restricts the performance of liquid phase cleaning. The CO_2 snow cleaning process also is believed to attach hydrocarbon film by dissolving hydrocarbon molecules in a temporal liquid CO_2 phase at the film-substrate interface (Whitlock, 1989). The dissolved film is then carried away by subsequent flow of snow and gas.

Operating Features

A complete system includes a CO_2 purifier, a pneumatic actuated head, and a microprocessor-based timing circuit. Several models of manual spray booths are available that provide a nitrogen-purged, heated, and monitored environment for CO_2 spraying that cost $10K to $15K. One commercial purifier is available in a 17 x 14 x 24 1/2 inch stainless steel cabinet. It weighs 135 lb and requires an energy supply of 6 A, 115 VAC, and 60 Hz.

Another commercially available purifier is capable of purifying CO_2 to a water content of less than 20 ppb by weight. In laboratory analyses of CO_2 before and after purification, the hydrocarbon content of 1800 ppb by weight was reduced to 3 ppb hydrocarbon; CO_2 with 140 ppb by weight halocarbons was purified to 1 ppb wt halocarbons. The purifier works on a 25% duty cycle, allowing use for 1 minute to every 3 minutes of recovery time. The snow gun consumes 0.6 lb of CO_2 per minute when used continuously.

If the dust or dirt particles removed by CO_2 snow cleaning are a hazard, they can be collected by an electrically charged curtain (Hoenig, 1990).

Application

CO_2 snow gently removes particles smaller than 10 microns in diameter down to 0.1 micron that are difficult to remove using high-velocity liquid nitrogen. It is used to remove light oils and fingerprints from mirrors, lenses, and other delicate surfaces, and from precision assemblies, without scratching the surface.

Uses of CO_2 snow range from hybrid circuitry to the optics industry.

CO_2 snow can clean hybrid circuitry and integrated circuits without disturbing the bonding wires. This unique ability cannot be duplicated by any other cleaning mechanism. In the disc drive industry, CO_2 snow is used to remove particles from discs without damage to the operation (Hoenig, 1990).

The process is used to remove paste fluxes in soldering. If the grease cannot be removed with CO_2 snow alone, a combination of CO_2 snow and ethyl alcohol is effective, followed by CO_2 snow alone to remove the impurities from the alcohol (Hoenig, 1990).

CO_2 is used to remove hydrocarbons and silicone grease stains from silicon wafers. Wafers artificially contaminated with a finger print, a nose print, and a thin silicone grease film were found to have surface hydrocarbon levels 25 to 30% lower after CO_2 snow cleaning than the original wafer surfaces (Sherman and Whitlock, 1990).

CO_2 snow cleaning is extremely effective.

Layden and Wadlow (1990) report a reduction of zinc orthosilicate concentration on a silicon wafer of more than 99.9% after cleaning by high-velocity CO_2 snow. Whitlock (1989) reports removal of greater than 99.9% for particles ranging from 0.1 to 0.5 micron diameter.

In the field of optics, CO_2 snow is used to clean the light-scattering particles and debris from the mirrors of the world's largest and most expensive telescopes.

CO_2 snow also is used to clean surfaces exposed to contaminants in air prior to surface analysis. The process was found to work better than solvents to clean vacuum components. Because the aerosol could penetrate narrow spaces, no disassembly was required, greatly shortening the time required for cleaning. Furthermore, CO_2 cleaning is effective on some plastic parts that cannot be cleaned by solvents (Layden and Wadlow, 1990).

Benefits

Some of the major beneficial aspects of CO_2 snow include

- CO_2 snow performs ultrapure cleaning of light oils down to submicron size on the most delicate, sensitive materials ranging from bonding wires to precision mirrors in telescopes.
- The CO_2 snow crystals generated by the snow gun are extremely gentle.
- The CO_2 snowflakes are adjustable to a wide range of size and intensity.
- The process does not create thermal shock, is nonflammable and nontoxic, and causes no apparent chemical reactions.
- Cleaning by CO_2 snow is noncorrosive and leaves no residue.
- CO_2 snow does not crack glass or other ceramics.
- No media separation system is needed, nor is there a media disposal cost.
- CO_2 snow can penetrate the nonturbulent area to dislodge contaminants and can be used on components without disassembly that otherwise must be disassembled because the aerosol penetrates narrow spaces.

Limitations

Potential hazards and limitations of CO_2 snow include

- Heavier oils, alone or mixed with light oils, may require chemical precleaning and/or heating to be completely removed.
- The CO_2 must be purified because of its tendency to dissolve contaminants from the walls of tanks in which it is stored. Purification equipment adds expense to the CO_2 snow cleaning system.
- When surfaces are excessively chilled by long dwell times, airborne impurities may condense and settle on the clean surface (Zito, 1990).
- CO_2 snow has low Mohs hardness and will not scratch most metals and glasses. However, hard particulates such as sand that may be present on a surface potentially could cause scratching when they are carried by the gas stream.

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Regulations Affecting Aqueous Cleaning Systems

The new Metal Products and Machinery effluent guideline will most probably affect you . . .

By John B. Durkee, II
President
Creative EnterpriZes
Lake Jackson, Texas

The proposed Metal Products and Machinery (MP&M) effluent guideline was signed on March 31, 1995, and was published in the Federal Register (FR) at the end of April. You can get a full copy of the proposed rule by downloading it from the EPA bulletin board at 703-821 4695 [8N1] as file MP&M.ZIP, from the FR as published, or by contacting the EPA administrator's office.

Does This Affect Me? What does it mean if I replace my vapor degreaser with an aqueous cleaning line? Your new aqueous cleaning line probably will be covered by this regulation if it is the first or a large source of process wastewater at your facility. However, it will not be covered if there are other sources of process wastewater, and discharge from the new aqueous cleaning line is only a modest part of the total discharge.

OK. So it Affects Me. What Does it Mean? The proposed regulation is performance-based and does not specify a method of compliance. Users must meet mass-based limits. This is distinctly different from the NESHAP for chlorinated solvents in that only certain "control combinations" can be used.

Generally you will use conventional wastewater treatment, chemical precipitation followed by clarification. Oily streams are treated with emulsion-breaking and oil skimming techniques. Cyanide-bearing wastewater goes through cyanide destruction with sodium hypochlorite. Chromium-bearing wastewater is treated to reduce hexavalent chromium to trivalent. Self-monitoring for cyanide must be conducted after cyanide treatment and before combining it with other streams. In-process flow reduction and recycling would also be used.

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TABLE I—Concentration Limits

Pollutant or Property mg/liter	Daily Maximum mg/liter	Monthly Avg. Maximum mg/liter
Aluminum	1.4	1.0
Cadmium	0.7	0.3
Chromium	0.3	0.2
Copper	1.3	0.6
Iron	2.4	1.3
Nickel	1.1	0.5
Zinc	0.8	0.4
Cyanide	0.03	0.02
Oil & Grease	35	17
TSS (total suspended solids)	73	36
One pH	Within 6.0 to 9.0	Within 6.0 to 9.0

The effluent limits represent the degree of effluent reduction attainable by applying the best practical control technology (BPT) currently available. Your permit limit will be determined by a concentration limit multiplied by a mass flow rate, and converted to mass units. The permit writer will use an appropriate process wastewater flow rate that may reflect your current values or less. For direct and indirect dischargers, the concentration limits are as shown in Table I.

What is the MP&M? The MP&M effluent guideline covers facilities that manufacture, maintain and rebuild finished metal parts, products or machines in the following industrial sectors: aircraft, aerospace, electronic equipment, hardware, mobile industrial equipment, ordnance, and stationary industrial equipment. This is Phase I of the implementation.

Seven additional sectors will be covered in 1999 as Phase II: bus and truck, office machines, household equipment, railroad, instruments, ships and boats, motor vehicles, and precious and non-precious metals.

Indirect discharges are those to a POTW (Publicly Owned Treatment Works); direct discharges are to surface waters. Existing indirect discharges of less than one million gal per year (4,000 gpd), per site, are exempt from this proposal. New indirect, and all direct discharges are covered by this proposal, at any flow rate.

For those cleaning parts in industry sectors covered by this regulation, the effect of this regulation depends on other operations that discharge water. The limit is by site. If you discharge water from spray cleaning large aircraft to a POTW, the discharge from the smallest cleaning station will be covered.

Alternately, larger discharges from aqueous cleaning machines probably will be covered now in the absence of any other site discharges, since the annual discharge volume will likely exceed one million gal. Remember, it is not the cleaning equipment being regulated, it is the water discharged from the site.

New discharges, direct or indirect, at any flow rate, will be covered. New means relative to the site (installation or building). And the definition of "new" is a judgment call for the permit writer, who will reference CFC 403.3.K.1.

Both new and existing facilities must meet technology-based limits. The limits are calculated using mass, which means "dilution is no longer the solution to pollution."

When is Compliance Necessary? Three years from the date the rule is finally promulgated, which will probably be September 30, 1999.

Why is the EPA Doing This? The purpose is to eliminate almost a million lbs of toxic pollutants discharged each year. The metals content of municipal sludge will be reduced, so POTWs do not have to landfill or incinerate the non-hazardous sludge.

Important aspects are fairness and not letting one type of pollution (ozone-depletion) be traded for another (water-pollution).

The EPA estimates that 75 pct of the affected facilities are small businesses that should not see a major economic impact. The EPA estimates direct and indirect dischargers will pay $50 and $127 respectively per incremental pound toxic equivalent.

VOX Populi. When published, you will have 90 days from the date of publication to comment on this proposal.

I expect significant comment about the concentration levels of metals, particularly aluminum, iron, and lead. The low levels given are seen in drinking water of fairly high quality. Typical wastewater treatment may not recover high levels of iron normally present in water, particularly when aggressive aqueous metal cleaning is done at high or low pH. The addition of alum often causes normal drinking water to have higher levels of aluminum than are allowed in this regulation. In that case, washing plastic would exceed the aluminum level in the permit. And lead, which is toxic, is not mentioned because there was no data on which to base a limit.

The oil and grease test is an extraction with Freon 113 (or hexane). It is likely there will be public comment about why a traditional TOC test cannot be used or substituted.

The oil and grease test may miss some detergent and solvent components of cleaning agents, and solubilized or emulsified soils. There will also be public comment about this test missing organic matter that is more soluble in water than in the extract.

The EPA will review public comment, and are scheduled to issue a final ruling in September, 1996. You should consider commenting. **PF**

Additional Copy?

To request an additional copy of this article, write on company letterhead to "Reprints," c/o PRODUCTS FINISHING, 6600 Clough Pike, Cincinnati, OH 45244.

OhioEPA

State of Ohio Environmental Protection Agency

STREET ADDRESS:
1800 WaterMark Drive
Columbus, OH 43215-1099

TELE: (614) 644-3020 FAX: (614) 644-2329

MAILING ADDRESS:
P.O. Box 1049
Columbus, OH 43216-1049

Vendors of Cleaning Solutions and Equipment
September 1995

The following are tables of vendors of cleaning solutions and equipment. These tables are a partial representation. If you wish to be added to the tables, please notify the Ohio EPA Office of Pollution Prevention in writing. These tables are not an endorsement or approval of these vendors by Ohio EPA.

Cleaning Solutions

Vendor	Aqueous	Semi-Aqueous		
		Hydrocarbon	Terpene	Alcohol
3D, Inc.	x		x	
ADF Systems, Ltd.	x			
Advanced Research Technologies		x		
Ambassador Marketing	x			x
Altos Engineering, Inc.	x			
ARCO Chemical Co.		x		x
Ardox	x	x	x	
Ashland Chemical	x	x		
BioChem Systems			x	
Blue Wave Ultrasonics	x			
Branson Ultrasonics Corp.	x			
Brulin Corporation	x	x		
Buckeye International, Inc.	x			
Calgon Corp.	x			
Chemical Solvents Inc.	x	x	x	x
Chem-Tech International	x	x		
Chemtronics Inc.	x			x
Circle-Prosco, Inc.	x	x	x	
Conceptronic, Inc.	x			x
CRC Industries, Inc.	x	x		
Creative Enterprises		x		
Crest Ultrasonics	x			
Dell-Chemical Systems Inc.	x			x
Delta Omega Technologies, Ltd.	x			
Dextrex Corp.	x	x		
Dow Chemical Co.	x	x	x	x
Dubois Chemical Inc.	x	x		x
Dynamold Solvents, Inc.	x	x		
Ecolink	x	x	x	
Eco-Systems			x	
Electolube Corp. USA	x			
Envirosolve	x		x	
ETUS, Inc.	x	x		
EXXON Chemical Co.		x		
EZE Products Inc.	x	x	x	
Fine Organics Corp.	x	x		

Cleaning Solutions continued

Vendor	Aqueous	Semi-Aqueous		
		Hydrocarbon	Terpene	Alcohol
Fremont Industries, Inc.	x			
Gray Mills Corp.	x	x		
Hubbard-Hall, Inc.	x	x		
Hurri-Kleen Corp.	x			
Inland Technologies	x	x	x	x
Insitu Environmental Chemical Co.	x			x
Kleer-Flo Co.		x		
Kyzen Corp.	x			x
Loctite Corp.		x	x	
MacDermid, Inc.	x			
Man-Gill Chemical	x	x		x
McDermott	x	x	x	x
North American Environmental Oil	x			
& Cleaning Supply Co.	x			
Oakite Products, Inc.	x			
Parker-Amchem	x			
Petroferm Inc.		x	x	
P-T Technologies, Inc.	x	x		
Qual Tech Enterprises, Inc.	x			
Ransohoff Co.	x			
Risson Group Inc.	x	x		
Rochester Midland Corp.	x	x		
Selig Chemical Industries	x	x		
SONICOR Instrument Corp.	x			
Storchem Inc.	x	x	x	
Sunshine Markers, Inc.	x			
Tech Spray Inc.	x	x	x	
Terpene Technologies Inc.	x	x	x	
Texo Corp.	x	x		
Ultrasound Fabrication, Inc.	x			
W.R. Grace & Co.	x			
Zip-Chem Products	x	x	x	x

Cleaning Equipment

Vendor	Aqueous	Semi-Aqueous	Media Blasting		Supercritical Fluids
			Plastic	CO2	
ACCEL	x	x			
AC Molding Compounds			x		
ADF Systems, Ltd.	x				
Alpheus Cleaning Technologies, Corp.				x	
Altos Engineering, Inc.	x	x			
American Metal Wash, Inc.	x				
Ardox	x				
Automated Blasting Systems Inc.			x		
Baron-Blakeslee, In.c	x	x			
Better Engineering	x				
Blackstone Ultrasonic, Inc.	x	x			
Blast-It-All			x		
Blue Wave Ultrasonics	x	x			
Bowden Industries	x				
Branson Ultrasonic Inc.	x	x			
Buckeye International, Inc.	x				
CF Technologies, Inc.					x
Chem-Tech International	x	x			
Cincinnati Industrial Machinery	x	x			
Clemco Industries Corp.			x		
Cold-Jet Inc.				x	
Composition Material Co., Inc.			x		
Conceptronic, Inc.		x			
Crest Ultrasonics	x	x			
Creative Enterprises	x				
Crest Ultrasonics	x				
Deflex Corp.					x
Dextrex Corp.	x	x			
Durr Industries, Inc.	x	x			
Ecolink	x	x			
Electonic Control Design, Inc.	x	x			
Empire Abrasive Equipment			x		
Environmental Recovery Resources, Inc.	x				
Envirosolutions Inc.		x			
EZE Products Inc.	x	x			
Finishing Equipment Inc.	x	x			
Gray Mills Corp.	x				
Hosty Equipment Corp.	x				
Jensen Fabrication Engineers, Inc.	x				
Kleer-Flo Co.	x	x			
Kleiber & Schulx, Inc.			x		
MacDermid, Inc.	x				
Man-Gill Chemical	x				
Maxi-Blast, Inc.			x		
Metal Dimensions			x		
MPC Industries			x		
Pangborn Corp.			x		
Parker-Amchem	x				
Paul and Griffin			x		
Proceco Inc.	x				

Cleaning Equipment continued

Vendor	Aqueous	Semi-Aqueous	Media Blasting		Supercritical Fluids
			Plastic	CO2	
Solidstrip, Inc.			x		
Stripping Technologies, Inc.			x		
Ransohoff Co.	x	x			
SONICOR Instrument Corp.	x	x			
Sonitech Inc.	x	x			
Stoelting Inc.	x				
Thierica	x				
Tiyoda Manufacturing USA, Inc.	x	x			
Ultrasound Fabrication, Inc.	x	x			
Unitech Industrial Inc.	x	x			
US Technology Corp.			x		

Addresses and Telephone Numbers

3D, Inc.
2053 Plaza Drive
Benton Harbor, MI 19022-2211
800-272-4326

ACCEL
1825 E. Plano Parkway
Plano, TX 75074-8129
214-424-3525

ADF Systems, Ltd.
P.O. Box 278
Humboldt, IA 50548
515-332-5400

Advanced Research Technologies
312 S. Vine St.
Park Ridge, IL 60068
708-696-9371

Altos Engineering, Inc.
6009 North 61 AVe.
Glendale, AZ 85301
602-931-8434

Ambassador Marketing
Route 1-Box 207
St. Davaid, AZ 85630
602-720-4310

American Metal Wash, Inc.
P.O. Box 265
360 Euclid Ave
Cannonsburg, PA 15317
412-746-4203

ARCO Chemical Co.
3801 West Chester Pike
Newton Square, PA 19073-2387
800-828-6627

Ardox
16961 Knott Ave.
LaMirada, CA 90638
714-739-2821

Ardox
16961 Knott Ave.
LaMirada, CA 90638
714-739-2821

Ashland Chemical
Industrial Chemical & Solvents
Division
5200 Paul Blazer Pkwy.
Dublin, OH 43017
614-790-3863

Baron-Blakeslee, Inc.
1500 W. 16th St.
Long Beach, CA 90813
800-548-4422

Better Engineering
8361 Town Center Court
Baltimore, MD 21236
800-229-3380

BioChem Systems
14452 W. 44th Ave.
Golden, CO 80403
800-777-7870

Blackstone Ultrasonic, Inc.
9 N Main St.
Jamestown, NY 14701
800-766-6606

Blue Wave Ultrasonics
Division of Alpheus Cleaning
Technologies Corp.
960 S. Rolff St.
Davenport, IA 52802
800-3763-0144

Bowden Industries
1004 Oster Dr. NW
Huntsville, AL 35816
205-533-3700

Branson Ultrasonic Inc.
41 Eagle Rd.
Danbury, CT 06810
203-796-0400

Brulin Corporation
P.O. Box 270
2920 Dr Andrew J. Brown Ave.
Indianapolis, PA 46206
317-923-3211

Buckeye International, Inc.
2700 Wagner Place
Maryland Heights, MO 63043
314-291-1900

Calgon Corp.
Chemical Technologies Group
P.O. Box 1346
Pittsburgh, PA 15230
800-955-0090

Chem-Tech International
1800 Diagonal Road, Suite 600
Alexandria, VA 22314
703-549-1001

Chemical Solvents Inc.
3751 Jennings Rd.
Cleveland, OH 44109
800-362-0693

Chemtronics Inc.
8125 Cobb Center Dr.
Kennesaw, GA 30144
404-424-4888

Cincinnati Industrial Machinery
P.O. Box 62027
Cincinnati, OH 45262
513-769-0700

Circle-Prosco, Inc.
2017 Yost Ave.
Bloomington, IN 47403
812-339-3653

Conceptronic, Inc.
6 Post Rd.
Portsmouth, NH 03801
603-431-6262

CRC Industries, Inc.
885 Louis Cr.
Warminster, PA 18974
215-674-4300

Creative Enterprises
3560 Springwood, Suite 811
Ponca City, OK 74604
405-765-0879

Crest Ultrasonics
P.O. Box 7266
Scotch Rd. - Mercer County Airport
Trenton, NJ 08628
800-441-9675

Dell-Chemical Systems Inc.
7119 E. Shea Blvd., Suite 106-224
Scottsdale, AZ 85254
602-951-5812

Delta Omega Technologies, Ltd.
7608 Hwy 90 W.
New Iberia, LA 70650
318-367-6400

Dextrex Corp.
4000 Town Center, Suite 1100
Southfield, MI 48175
313-358-5800

Dow Chemical Co.
Advanced Cleaning Systems
2020 Dow Center
Midland, MI 48674
800-447-4369

Dubois Chemical Inc.
511 Walnut St.
Cincinnati, OH 45212
513-762-6839

Durr Industries, Inc.
10301 Enterprise Dr.
Davisburg, MI 48360
810-625-5400

Dynamold Solvents, Inc.
2905 Shamrock Ave.
Fort Worth, TX 76107
817-335-0862

Ecolink
1481 Rock Mountain Blvd.
Stone Mountain, GA 30083
800-886-82403272

Eco-Systems
345 Beckett Place
Grover Beach, CA 93433
800-368-3700

Electolube Corp. USA
8200 Saint James Ave.
Elmhurst, NY 11373
718-565-5200

Electonic Control Design, Inc.
4287-A SE International Way
Milwaukie, OR 97006
800-323-4548

Environmental Recovery
Resources, Inc.
P.O. Box 36
South Salem, NY 10590
914-533-6175

Envirosolutions Inc.
335 Post Rd. W.
Westport, CT 06880
203-454-5902

Envirosolve
1840 Southside Blvd.
Jacksonville, FL 32216
904-724-1990

ETUS, Inc.
1511 Kastner Place
Sanford, FL 32771
407-321-7910

EXXON Chemical Co.
P.O. Box 3272
Houston, TX 77253
800-526-0749

EZE Products Inc.
P.O. Box 5744
Greenville, SC 29606
800-255-1739

Fine Organics Corp.
P.O. Box 687
205 Main St.
Lodi, NJ 07644-0687
800-526-7480

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3640 Kennebec Dr.
St. Paul, MN 55122
612-452-1860

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4400 Valley Industrial Park
Shakopee, MN 55379
612-445-4121

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Chicago, IL 60613
312-248-6825

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27 Inverness Way E.
Englewood, CO 80112-5796
303-792-5200

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P.O. Box 790
Waterbury, CT 06725
800-648-3412

Hurri-Kleen Corp.
P.O. Box 29
Trussville, AL 35173
250-655-8808

Inland Technologies
401 E. 27 St.
Tacoma, WA 98421
800-552-3100

Insitu Environmental Chemical Co.
8402 E. Redwing Rd.
Scottsdale, AZ 85250-5740
602-948-9209

Jensen Fabrication Engineers, Inc.
P.O. Box 362
East Berlin, CT 06023
203-828-6516

Kleer-Flo Co.
15151 Technology Dr.
Eden Prairie, MN 55344
800-328-7942

Kyzen Corp.
413 Harding Industrial Dr.
Hashville, TN 37211
800-845-5524

Loctite Corp.
705 N. Mountain Rd.
Newington, CT 06111
800-562-0560

MacDermid, Inc.
245 Freight St.
Waterbury, CT 06702
230-575-5719

Man-Gill Chemical
23000 St. Clair Ave.
Cleveland, OH 44117
800-328-9745

McDermott
2053 APlaza Dr.
Benton Harbor, MI 49022
800-272-5326

North American Environmental Oil
& Cleaning Supply Co.
270A route 46, Suite B1
Rockaway, NJ 07899
201-627-0722

Oakite Products, Inc.
50 Valley Rd.
Berkeley Heights, NJ
07922
800-526-4473

P-T Technologies, Inc.
108 4th Ave. S.
Safety Harbor, FL 34695
800-441-7874

Parker-Amchem
32100 Stephenson Highway
Madison Heights, MI 48071
800-521-6895

Petroferm Inc.
5415 First Coast Highway
Fernandina Beach, FL 32034
904-261-8286

Proceco Inc.
7300 Tellier St.
Montreal, Quebec
Canada, H1N 3T7
514-254-8494

Qual Tech Enterprises, Inc.
1485 Bayshore Blvd.
San Francisco, CA 94124
415-467-7887

Ransohoff Co.
N 5th St at Ford Blvd.
Hamilton, OH 45011
800-248-9274

Risson Group Inc.
13349 Michigan Ave.
Dearborn, MI 48126
313-581-2620

Rochester Midland Corp.
333 Hollenbeck St.
Rochester, NY 14621
716-336-2200

Selig Chemical Industries
P.O. Box 43106
840 Selig Dr. SW
Atlanta, GA 30378
404-691-9220

SONICOR Instrument Corp.
100 Wartburg Ave.
Copiague, NY 11726
516-842-3344

Sonitech Inc.
239 E. Stephenson St.
Freeport, IL 61032
815-235-2400

Stoelting Inc.
502 Highway 67
P.O. Box 127
Kiel, WI 53042
414-894-2293

Storchem Inc.
3600 Billings Court, Suite 110
Burlington, Ontario
Canada L7N 3N6
416-639-9700

Sunshine Markers, Inc.
15922 Pacific Coast Highway
Huntington Harbor, CA 92649
800-228-0709

Tech Spray Inc.
P.O. Box 949
Amarillo, TX 79105-0949
800-858-4043

Terpene Technologies Inc.
1325 Midtown Tower
Rochester, NY 14604
716-423-0670

Texo Corp.
2801 Highland Ave.
Cincinnati, OH 45212
513-731-3400

Thierica
900 Clancy Ave.
Grand Rapids, MI 49503
616-458-1538

Tiyoda Manufacturing USA, Inc.
1613 Lockness Place
Torrance, CA 90501
310-539-5471

Ultrasound Fabrication, Inc.
1 Maple St.
Shelton, CT 06484
203-924-1624

Ultrasound Fabrication, Inc.
1 Maple St.
Shelton, CT 06484
203-924-1624

Unitech Industrial Inc.
P.O. Box 330
16 South Ave.
Wappingers Falls, NY 12590
800-277-5522

W.R. Grace & Co.
Metalworking Fluids Group
55 Hayden Ave.
Lexington, MA 02173
617-861-6600

Zip-Chem Products
1860 Dobbin Dr.
San Jose, CA 95133
800-648-2661

AC Molding Compounds
So. Cherry St.
P.O. Box 425
Wallingford, CT 06492
800-523-2262

Automated Blasting Systems Inc.
46 Schweir Rd.
South Windsor, CT 06074
203-528-5525

Blast-It-All
P.O. Box 1615
Salisbury, NC 28145-1615
800-535-2612

Clemco Industries Corp.
One Cable Car Dr.
Washington, MO 63090
314-239-0300

Composition Material Co., Inc.
1375 Kings Highway East
Fairfield, CT 06430
800-262-7763

Empire Abrasive Equipment
2101 W. Cabot Blvd.
Langhorne, PA 19047-1893
215-752-8800

Kleiber & Schulx, Inc.
2017 New Highway
Farmingdale, NY 11735
516-293-6688

MPC Industries
638 Maryville Pike, S.W.
P.O. Box 9246
Knoxville, TN 37920
800-340-7523

Maxi-Blast, Inc.
630 E. Bronson
South Bend, IN 46601
800-535-3874

Metal Dimensions
4720 District Blvd.
Vernon, CA 90058
213-582-1955

Pangborn Corp.
P.O. Box 380
Hagerstown, MD 21741
800-638-3046

Paul and Griffin
907 Cotting Lane
Vacaville,CA 95688
707-447-7000

Solidstrip, Inc.
601 Interchange Blvd.
Newark, DE 19711
800-677-4568

Stripping Technologies, Inc.
2949 E. Elvura Rd.
Tuscon, AZ 85706
800-741-0501

US Technology Corp.
220 Seventh St., SE
Canton, OH 44702
800-634-9185

Alpheus Cleaning Technologies,
Corp.
9105 Milliken Ave.
Ranco Cucamonga, CA 91730
714-944-0055

Cold-Jet Inc.
455 Wards Corner Rd., Suite 100
Loveland, OH 45140
513-831-3211

CF Technologies, Inc.
1 Westinghouse Plaza, Suite 200
Hyde Park, MA 02136-2059
(617) 364-2500

Deflex Corp.
3058 N. Lima St
Burbank, CA 91504
818-556-3335